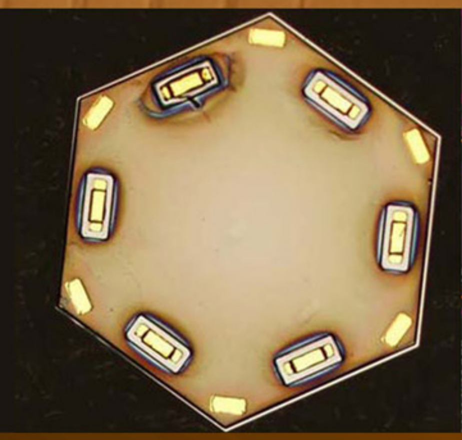
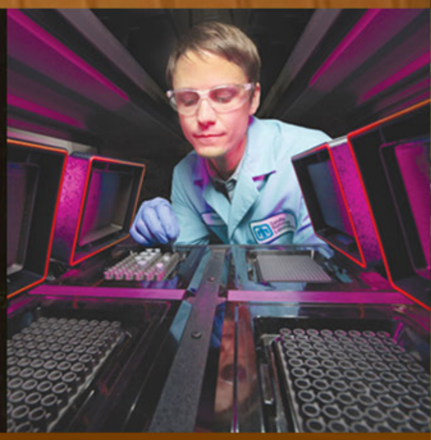
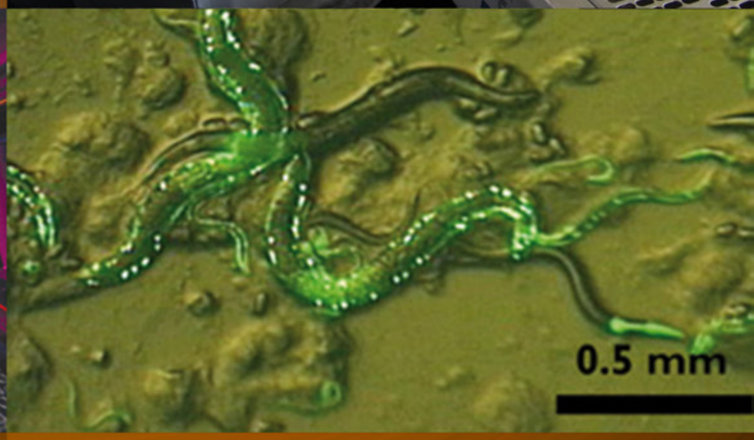
LABORATORY DIRECTED RESEARCH AND DEVELOPMENT

LDRD

ANNUAL REPORT 2011







SAND 2012-2254P

Sandia National Laboratories

NNSA National Nuclear Security Administration

Cover photos:
Upper Left: Sandian Jeff Koplow adjusts an earlier prototype of his Air Bearing Heat Exchanger (Project 151304). The technology — also known as the "Sandia Cooler" —significantly decreases the energy needed to cool processor chips in datacenters and large-scale computing environments.

Center: Three single atoms captured and imaged using a diffractive optical element trap (Project 152501), behind which is a Sandia-developed ion trap used in Project 148549.

Right: Harry S. Truman Fellow Carlee Ashley pipettes a solution associated with her virus-like particles (Project 151379), protein nano-aggregates that can deliver multiple vaccine-stimuli to the immune system (thereby making them potentially useful to combat bioweapons attacks) and which can also deliver therapeutics to cancer cells.

Bottom Strip: Left: Dual junction InGaP/GaAs photovoltaic cell with backside contacts (Project 141519). *Middle:* Stan Langevin optimizes DNA hybridization conditions in conjunction with the RapTOR Project's (142042) ability to detect rare pathogen DNA or RNA. *Right:* Nematodes fluoresce in their role as biodetectors of residual live viruses (Project 130755).

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Abstract

This report summarizes progress from the Laboratory Directed Research and Development (LDRD) program during fiscal year 2011. In addition to a programmatic and financial overview, the report includes progress reports from 427 individual R&D projects in 12 categories.

National Nuclear Security Administration

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

SAND 2012-2254P
March 2012

LDRD Annual Report Staff:

Sandia National Laboratories

Hank Westrich
Sheri Martinez
Vin LoPresti
Donna Chavez
Yolanda Moreno
Carol Ashby
Rachel Silva

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Sandia National Laboratories' FY 2011 Laboratory Directed Research and Development (LDRD) Program:

Discretionary Research and Development For The Future of The Labs

J. Stephen Rottler, Vice President of Science, Technology, and Engineering and Chief Technology Officer

As authorized by Congress, the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories (SNL) is critical to maintaining the vitality of our Labs in mission-critical science and engineering (S&E) disciplines. As SNL's sole discretionary R&D program, LDRD enables our technical staff to pursue innovative, high-risk and potentially high-value research and development (R&D) for a range of difficult S&E challenges facing our nation. Through LDRD, the Labs can pursue game-changing S&E, develop the next generation of mission-critical capabilities — thereby impelling the laboratories' mission. Simultaneously, these research endeavors advance the frontiers of science and engineering, discovering innovative solutions for emerging technical surprises. Innovation in these arenas is crucial to our overall mission of providing "exceptional service in the national interest."

Sandia LDRD projects provide both direct and indirect benefit to the national security missions of the Laboratories and DOE/NNSA. LDRD is a key component for the development and use of science and engineering capabilities currently employed by the nuclear weapons program, such as fundamental and applied research in materials science to create MEMS-enabled integrated optical circuits, vapor-phase lubrication technology for advanced surety components, new high-energy neutron spectrometers. In addition, LDRD supports crosscutting R&D in nonproliferation, alternative energy, climate, infrastructure, and cyber security arenas to seek innovative technical solutions for these emerging S&E challenges facing our nation in the Twenty-First Century and beyond. These discretionary investments often provide benefits to multiple missions, frequently demonstrating a broader impact, unanticipated in the initial proposal.

The FY 2011 LDRD program sponsored 427 projects costing $163 M. This annual report offers an overview of the LDRD projects that were ongoing in FY 2011, highlighting only a few examples to demonstrate the scope of LDRD investments. The program overview and project summaries provide a window into the program's S&E innovation and its potential for impact on national imperatives.

Sandia FY 2011 Program Overview

Program Purpose

With the current and future missions of the Department of Energy/National Nuclear Security Administration (DOE/NNSA) as our guiding principle, the Laboratory Directed Research and Development (LDRD) program at Sandia National Laboratories (Sandia) supports our broad scope of national security missions in a forward-looking, proactive fashion. Per Congressional intent (P.L. 101-510) and DOE guidance (DOE Order 413.2B), the Sandia National Laboratories' LDRD program is crucial to maintaining our scientific and technical vitality and enhancing our ability to address current and future national security missions. More explicitly, Sandia's goals for the LDRD program are as follows:

- Advance the frontiers of science and technology
- Enable innovative S&T in support of our national security missions
- Nurture new, differentiating capabilities essential to Sandia's missions

Within the LDRD program, Sandia staff have the opportunity to pursue leading edge research ideas, hone their technical skills, develop their professional leadership, and advance the state of the art of ST&E in support of the Labs' enduring national security missions.

With a budget of $163 M for 427 projects in FY 2011, the program has underwritten a myriad of high-risk science, technology, and engineering (ST&E), often in collaboration with scientists and engineers in academia, corporations and at other DOE laboratories. It has yielded outcomes contributing to nuclear, homeland, cyber, infrastructure, energy, climate, health, and intelligence security — in areas as diverse as nuclear weapons systems, novel sensor concepts and technologies, quantum science and technology, nanotechnology, metamaterials, computational modeling and simulation, carbon-neutral energy, molecular biology and biomedicine, and cognitive science. In turn, the results of this research support DOE missions in nuclear security, energy security, environmental responsibility, and scientific discovery and innovation.

PROGRAM DESCRIPTION

PROGRAM ORGANIZATION AND STRUCTURE: Responsibility for the Sandia LDRD program rests with the Sandia President, who delegates policy and process authority to the Chief Technology Officer (CTO). Reporting to the CTO, the LDRD Office is responsible for day-to-day program management, process development, final proposal review, monitoring of outcomes, reporting to the responsible NNSA entities, and when appropriate, conducting periodic operational program reviews for the purpose of recommending program and process amendments.

Since FY 2007, LDRD strategic investments have been based on a balanced portfolio of stable funding targets for major investment categories, driven by the strategic intent of the LDRD portfolios. There are four major investment categories, called Program Areas (PAs): Science, Technology and Engineering Foundations (ST&E), Mission Technologies (MT), Grand Challenges (GC) and Corporate Investments (CI). Twelve investment areas (IAs) are organized under these four global categories as described below (note that more-detailed descriptions of each IA, with summarized exemplary projects, can be found as sectional introductions within the body of this document, prior to the corpus of project reports for that particular IA; see pages 23, 111, 217, 269, 313, 418, 500, 555, 618, 644, 659, and 669).

PROGRAM AREA: Mission Technologies (MT)

The Mission Technologies Program Area seeks to create and nurture the ability to provide innovative future solutions for DOE and work for others (WFO) sponsors of the Laboratories' mission areas, creating or accelerating the development of the needed technologies for national security issues. The four Mission Technologies IAs align with the Laboratories' Strategic Management Unit (SMU) structure

- **Defense Systems and Assessments (DSA):** Develop innovative, technology-based systems solutions to the most challenging issues facing the national security community.
- **Energy, Climate, and Infrastructure Security (ECIS):** Develop and apply differentiating technologies in three lines of business: Fuel and Water Systems, Nuclear Energy, and Global Security to address critical national security needs.
- **International, Homeland, and Nuclear Security (IHNS):** Provide scientific, technological, and systems solutions that will secure our nation against high-consequence terrorist threats and national incidents.
- **Nuclear Weapons (NW):** Develop and create products and capabilities that incubate science, technology or engineering solutions for any of the possible NW mission needs.

PROGRAM AREA: Science, Technology, and Engineering Foundations

The Science, Technology, and Engineering Foundations Program Area seeks to anticipate and provide for the future ST&E needs of the Laboratory, fostering our science base as a means to further developing the critical existing and future ST&E capabilities that the SMUs need to support our national security missions. The five ST&E Foundations IAs are:

- **Enable Predictive Simulation (EPS):** Sponsor innovative research and development that revolutionizes the knowledge base and capabilities necessary for predictive simulation of complex problems.
- **Nanoscience to Microsystems (NTM):** Discover new phenomena at the nanoscale; and create or prove new concepts, materials, devices, processes, components, subsystems, and systems.
- **New Directions (ND):** Develop new competencies in the two thematic areas of Biological Science and Technology, and Cognitive Science and Technology.
- **Science of Extreme Environments (SEE):** Create new knowledge that enables revolutionary advances in the areas of high energy density physics, radiation sciences, pulsed power, and fusion energy for National Security needs.
- **Cyber Security S&T (CS):** Build the science and engineering foundations needed to address key cyber security challenges in trust, resilience, and attribution.

PROGRAM AREA: Corporate Investments

Corporate Investments support the strategic needs of Sandia as a national laboratory, nurturing our workforce, developing external partnerships, and seeking breakthrough science and technology.

- **Strategic Partnerships:** Support workforce development through strategic science and engineering initiatives, and strategic university partnerships.
- **Seniors' Council:** Nurture very high risk that might lead to revolutionary ST&E that would be important to support long-term mission needs, and directed opportunities for innovative R&D.
- **Early Career R&D:** Two-year-funded projects designed to assist new staff members in initiating research programs. Funds high-risk, potentially high-value research that enables the missioins of Sandia, with a specific focus on the rapid integration of early career Ph.D. staff into the Sandia workforce.

PROGRAM AREA: Grand Challenges

Grand Challenges address some of the most difficult problems facing our nation, using larger (>$1.3M project) multidisciplinary teams to create significant S&T advances that lead to unique or differentiated capabilities not likely to be duplicated elsewhere.

BUDGET: Figure 1 illustrates a breakdown of the FY 2011 portfolio by program area cost. Early Career R&D costs are distributed among the IAs in ST&E and MT.

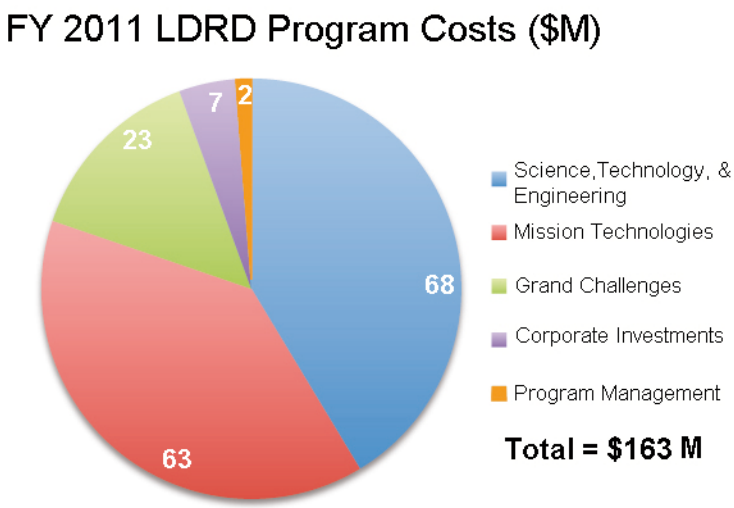


Figure 1: FY 2011 portfolio by program area cost

FUNDING PROCESS: Each Investment Area (IA) manager selects a small group of experienced managers and senior staff to manage their IA processes, including writing the call, reviewing proposals and evaluating project progress. In addition, the IA team works with the PI and project manager in leveraging project outcomes. Each IA has a representative on the Senior Working Group (SWG), where the lead IA representative (or alternate) meets monthly with other IA members to share information, discuss processes, and suggest overall program improvements.

The process for selecting LDRD projects is a formal process described as follows:

The Sandia Chief Technology Officer, in collaboration with the Executive Office, identifies the LDRD IA structure and budget targets.

- The Laboratories' call for ideas is written by the IAs, and describes the strategic intent of their IA and their alignment with their SMU's strategic plan.
- Interested employees submit 500-word "ideas" on-line to the appropriate investment areas for evaluation. Grand Challenge ideas are twice the length of a normal idea.
- The IA teams look for ideas that describe leading edge R&D, have potential impact on future activities, and are aligned with Sandia's strategic missions.
- The IA then requests full proposals for internal peer review. A proposal that details progress and tasks for the coming year is also needed for all continuation LDRDs. Proposal length varies with budget: at <$1300 K, a 5-page proposal is written in addition to the data sheet; and for projects exceeding $1300 K (i.e., Grand Challenge), a 20-page proposal is submitted in addition to the data sheet.
- Independent technical and programmatic appraisals are conducted on each new proposal. Continuation proposals are reviewed annually. The IA teams then rank the proposals in order of funding preference, and select projects according to budget targets.
- The LDRD office reviews and submits appropriate project summaries (i.e., data sheets) to the Sandia Site Office (SSO) for individual concurrence.

- The LDRD program office then prepares the annual program plan for review and approval by the Chief Technology Officer, and approval by SNL's Executive Office.

For FY 2011, 857 ideas were submitted, from which 241were invited to submit new (initial-funding) proposals, and 108 of these proposals were approved for funding, a final funding rate of 12.6% (108 of 857 ideas).To these were added 89 new Early Career R&D projects, and 36 other late starts, for a total of 233 new projects. These 233 newly funded projects were added to 194 continuing projects yielding a total of 427 LDRD projects funded for the fiscal year.

PROGRAM IMPROVEMENTS: There were minor changes to the FY 2011 LDRD program, one of which was improved proposal templates to assist the principal investigators (PIs) in providing the needed information for proposal review, selection, and concurrence. Another was an electronic module added to our LDRD applications that allows the SSO to access our LDRD website to facilitate electronic review and concurrence of all proposals. Finally, the Cyber S&T IA was added to the ST&E Foundations program area because this S&T area was deemed to be critical for SNL's support of national security missions. In FY 2011, we coordinated a self-assessment that indicated staff concerns primarily in the area of transparency and feedback. Based upon the results of this self-assessment, several more significant process changes will be implemented for the FY 2012 LDRD Program.

PORTFOLIO DESCRIPTION:

Project Size: Of the 427 projects active in FY 2011, 233 were newly funded, in their first year, while 194 were continuing in their second or third years. The FY 2011 project size, by budget, is shown in Figure 2.

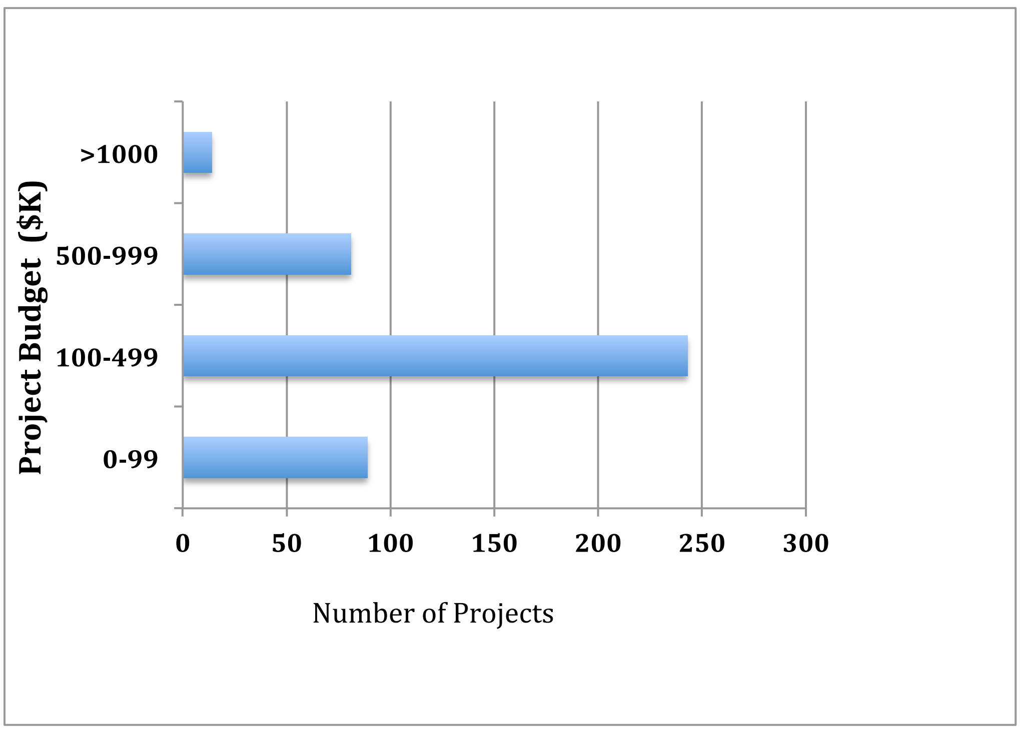


Figure 2. LDRD project size distribution, by budget: FY 2011

Mission Relevance: LDRD projects are chosen for their technical quality, their differentiating and programmatic value to SNL, and their relevance to DOE/NNSA's missions (nuclear security, energy security, environmental remediation, and scientific discovery and innovation), as well as the national security missions of the Department of Homeland Security, the Department of Defense, and Other Federal Agencies. As a result, the scientific advances and technology innovations from LDRD provide multiple benefits to all Sandia stakeholders, consistent with Congressional intent and our Laboratories' strategic goals. Figure 3 shows the mission relevance of the FY 2011 LDRD portfolio, and in particular, the broad support for a suite of current and planned national security missions for that portfolio. This information, provided by the IA managers during the FY 2011 portfolio selection, is not expected to change in the near future, barring any dramatic change in SNL strategic thrusts or LDRD funding levels. The dollar amounts total more than 100 percent of the total FY 2011 budget since many projects impact and have relevance to more than one mission area.

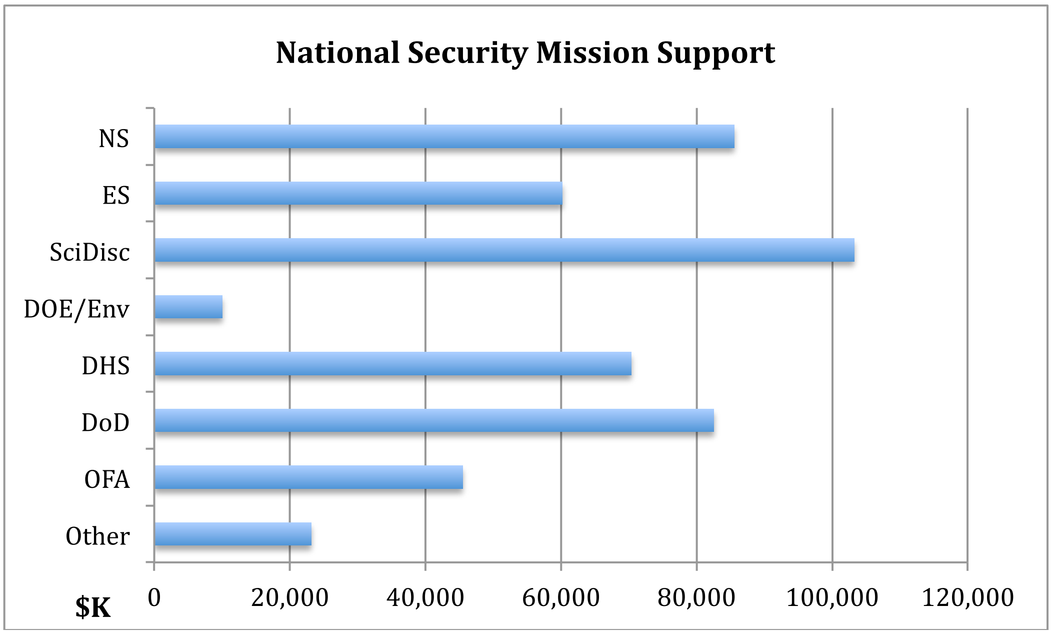


Figure 3. FY 2011 LDRD portfolio supports multiple mission challenges; DOE missions: Nuclear Security (NS), Energy Security (ES), Scientific Discovery (SciDisc), Environmental Responsibility (DOE/Env); and Department of Homeland Security (DHS), Department of Defense (DoD), Other Federal Agencies (OFA), and other agencies (Other).

Project Strategic Intent Distribution: The LDRD program supports a range of R&D activities from fundamental research through proof-of-principle studies, and to a certain extent, even field demonstrations. In this context, each project is accorded a strategic designation of either Discover, Create, or Prove (D, C, or P). The intent of "Discover" projects is the creation of new understanding or knowledge. "Create" projects pursue the innovative application or combination of new or existing knowledge in a unique fashion, in order to create a novel solution to a problem, or to provide a revolutionary scientific, technological, or engineering advance. "Prove" projects pursue the validation of a prospective innovation or concept in a real-world environment, in a fashion that reduces unknowns and uncertainties. In addition to the balanced portfolio principle of stable funding targets for major investment categories (Figure 1), the program also attempts to maintain a balanced portfolio with respect to project strategic intent. This DCP balance for FY 2011, is shown in Figure 4.

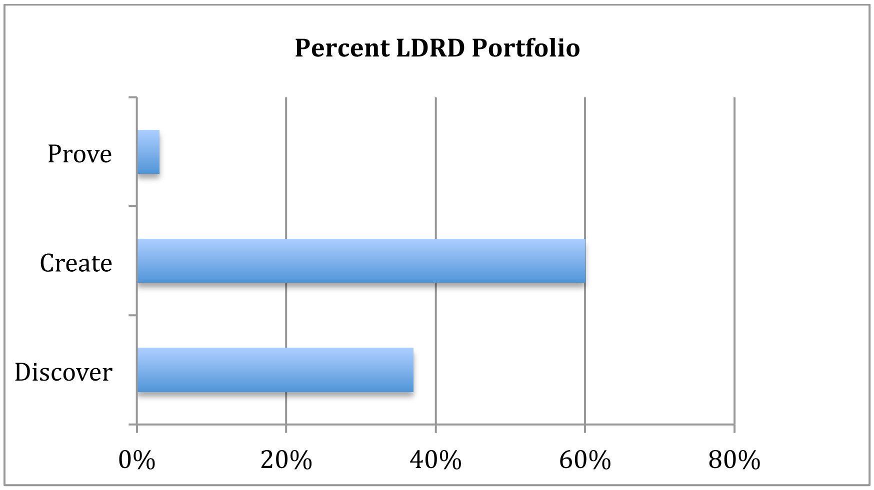


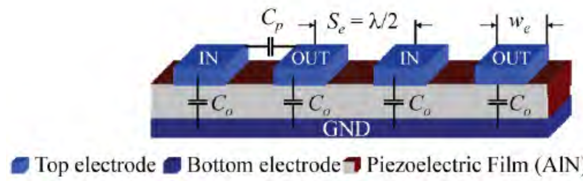
Figure 4. The DCP strategic intent for the FY 2011 LDRD portfolio

EARLY CAREER R&D (ECRD): Initiated in FY 2010, the Early Career R&D (ECR&D) element of the LDRD Program makes a maximum of $500K ($250K/yr) of LDRD funding available for a two-year project, to any Ph.D.-recipient technical staff member whose employment at Sandia commenced after October 1, 2010. The program continued into FY 2011, funding 89 new projects, and 21 continuing projects initiated in FY 2010. ECRD is designed to smooth transition into the Sandia workforce, enabling them to focus on creative activity, while simultaneously acclimating them to the national laboratory environment, with its dual focus on R&D and programmatic work. The LDRD Program Office published a brochure in April of 2011 delineating the research activities and experiences of the initial cohort of Early Career LDRD funding recipients, entitled, *Blazing a Creative Research Path: Sandia's LDRD Early Career Program* (SAND 2011-2176P). In addition, two Early Career Days were held to feature program research outcomes, the first, a symposium in December 2010, the second, a poster session in September 2011.

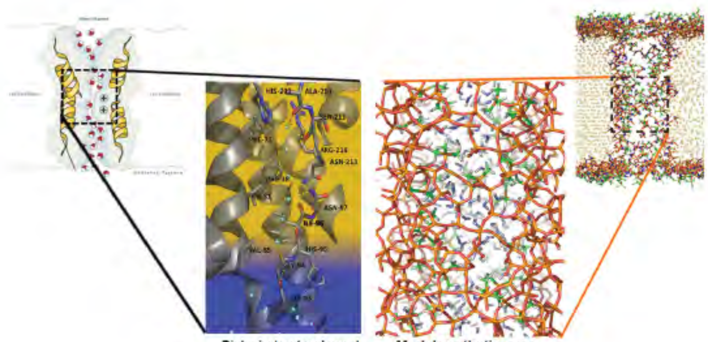
PROGRAM PERFORMANCE:

LDRD creates and builds new knowledge and novel technologies that develop new capabilities and produce major scientific advancements through leading edge R&D. Supporting evidence includes success stories and news coverage, awards and recognition, as well as statistical measures of outputs such as publications and intellectual property. A few examples are provided below.

FY 2011 Awards and Global Recognition:



In 2011, Sandia received four R&D100 Awards, of which two had their roots in LDRD projects. In the arena of energy and cyber security, the winner, *Microresonator Filters and Frequency References,* developed a miniature acoustic resonator allowing hundreds of filters and oscillators covering a wide range of frequencies to be collocated on a single chip, produced by standard integrated circuit methods, offering higher performance and frequency diversity in a very small package that will serve as a key element in next-generation cell phones and other wireless devices, enabling reduced size with an improvement in functionality.

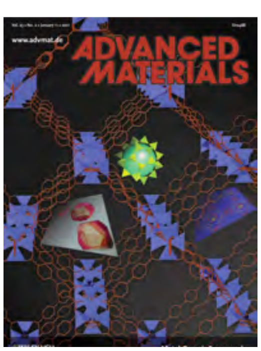

Biological water channel (crystal structure) (www.nobelprize.org)
Model synthetic pore (simulation studies)

In the arena of energy and infrastructure security, the *Biomimetic Membranes for Water Purification* winner designed chemically modified filtration membranes that mimic the proteins in the membranes of living cells — the channels for salts (sodium, potassium, calcium, etc.) and water (aquaporins) that allow water and the (salts ions) dissolved in it to be separately transited from outside a cell to inside or vice-versa. Such membranes can offer ten times increased performance at purifying water that is either brackish or contaminated, in order to produce clean drinking water, one of the 21st Century's most daunting problems, and one closely connected to energy security, since it requires energy to filter water through membranes.

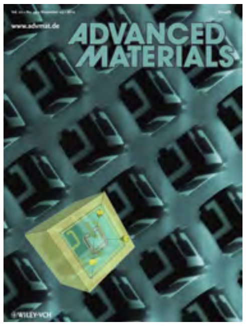
Scholarly Publications Featured on Journal Covers

Research directly tied to LDRD FY 2011 Funding:

The impact of LDRD-funded research at Sandia is aptly illustrated by the recognition accorded Sandia scholarly publications deriving from LDRD research. "The Targeted Delivery of Multicomponent Cargos to Cancer Cells by Nanoporous Particle-Supported Lipid Bilayers," by Harry S. Truman Fellow Carlee Ashley et al., including authors from both the laboratory of Sandia Laboratory Fellow, Jeff Brinker and from the University of New Mexico, University of California-Davis, University of Florida, and University of Waterloo (Ontario) describes a method for the creation of protocells. These are lipid-bilayer encapsulated silica-core nanoshells, whose potential for the delivery of multi-chemotherapeutic agents for one-dose killing of cancer cells is a creative leap forward in the field of cancer biomedicine. It captured the May 1, 2011 cover of the prestigious *Nature Materials.*

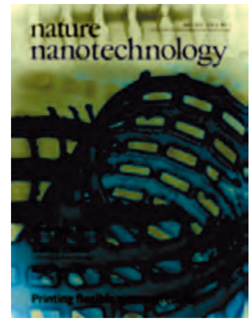


The article "Metal-Organic Frameworks: A Rapidly Growing Class of Versatile Nanoporous Materials" captured the cover of January 2011 *Advanced Materials*, reviewing the myriad civilian and national defense uses for this remarkable class of materials for whose development and characterization Sandia is justly awarded a significant share of the credit.



A team of Sandia researchers reported on its 3D metamaterials research, of enough significance to garner the cover of the November 24, 2010 issue of *Advanced Materials*, illustrating a colorized electron micrograph of so-called split-ring resonator metamaterials.

In related work, a printing technology capable of forming large-area, negative-index metamaterials was deemed an important enough advance to merit the July 2011 cover of *Nature Nanotechnology*.



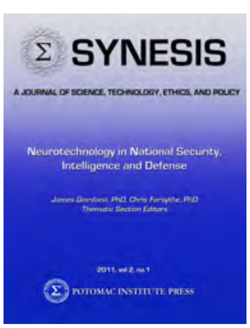
Research with roots in prior LDRD funding

The January 2011 issue of *Physica Status Solidia* reviewed the field of solid-state lighting, tapping the expertise of one of the Sandia pioneers in projects originally funded by Sandia LDRD and later by DOE, with Sandia serving as head of DOE's National Center for Solid State Lighting.

A team from Sandia, Lawrence Berkeley National Laboratory, and the University of California-Berkeley (essentially members of DOE's Joint Bioenergy Institute [JBEI]), captured the cover of November 15, 2010 issue of *Analytical Chemistry* with a microfluidic-chip-based assay for rapid and precise characterization of glycans and xylans resulting from biomass hydrolysis in a fashion 10-fold faster than high-performance liquid chromatography (HPLC).

A team of authors led by Sandia LDRD nanoelectronics researchers reviewed the field of processing technologies for thin films in capacitor applications in the December 2010 issue of the *Journal of the American Ceramics Society*. This is a research area supported by several past LDRD projects.

This research by Sandia technical staff on a specific example of polyoxometalate (POM)-like chemical behavior is underpinned by LDRD-funded research in the general area of POM chemistry. It captured the cover of the May 2, 2011 *European Journal of Inorganic Chemistry.*



Various LDRD-supported research in the area of cognitive sciences and their relevance to national security form some of the backdrop to the review article introducing this 2011 issue of the journal *Synesis*.

These examples are indicative of the impact resulting from LDRD investments in a diversity of national security areas, from materials science to microelectronics to energy conservation, biothreat detection, and improved healthcare strategies, each of them constituting a major contribution to its field, many of them nurturing the scientific growth of the next generation of US scientists and engineers.

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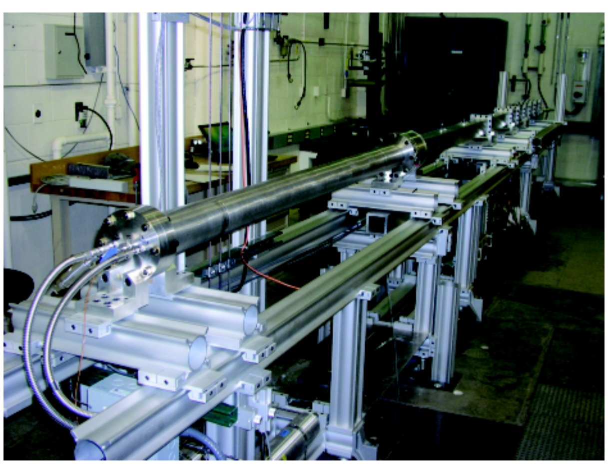
ENABLE PREDICTIVE SIMULATION INVESTMENT AREA

Computational modeling and simulation is the bailiwick of this investment area, funding research into computational activity that has the capability to both confirm and globalize experimental results, as well as to guide future experimentation and scientific intervention into national and global challenges. From models of material failure probabilities and explosive dynamics, to modeling water systems in semi-arid regions, to clarifying the properties of matter at the nanoscale, to new designs for computational memory, this IA's reach across Sandia's mission areas is quite extensive.

Experimental Characterization of Energetic Material Dynamics for Multiphase Blast Simulation

Project 130740

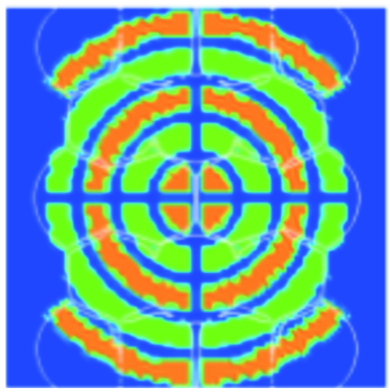
This project is combining experimentation and modeling to more-accurately unfold the details of energetic materials detonation including vulnerability of weapons and structures to nearby explosions, blast mitigation, improvised explosive device (IED) protection, and enhanced blasts. The early stages of detonation are particularly poorly understood, largely because of the initial tightly packed density of the particles. Common measurement methods have been unable to accurately diagnose these events. Hence, this project's activities have included construction of a multiphase shock tube that can drive a shock front into a particle/gas mixture, then measure the motion of the densely packed particles within the expanding gas. The project has developed novel x-ray diagnostics for particle-tracking velocimetry. By providing these crucial new physical data, these results will assist in increasing the fidelity of algorithms used to simulate blasts for a variety of national security applications, thereby improving computational simulation of explosions. This has already resulted in revised physical understanding of previously published data. Applications are numerous within the DOE complex and other federal agencies.



Photograph of the multiphase shock tube designed and built in this project

Nanomanufacturing: Nanostructured Materials Made Layer-by-Layer
Project 130741

Anticipating what prognostications have predicted to be a one-trillion dollar industry by 2015, this project is expediting — through modeling and simulation — benchtop to manufacturing scaleup for processes that will allow efficient manufacturing of microelectronics, photovoltaics, and other nanostructured materials. Project success is critical for broadening Sandia's advanced simulation and computing (ASC)-class software for impact in nanoengineering. This is the one of only a few efforts to bridge the plethora of Sandia and DOE-complex S&T nanoscience activities to the manufacturing sector, and hence, is crucial to US manufacturing competitiveness in forthcoming years. This includes the understanding that the greatest promise for high-volume manufacturing lies in age-old coating and imprinting operations. For materials with tailored nanometer-scale structure, imprinting/embossing must be achieved at high speeds (roll-to-roll) and/or over large areas (batch operation) with feature sizes less than 100 nm.



Simulation of multiple liquid drops (edges denoted by white lines) that have spread under forces of template imprinting. The template consists of a circular pattern of patches containing holes of various radii. The orange and green colors denote areas of the template that have filled with liquid to varying degrees, die to differences in the hole radii.

Enable Predictive Simulation Investment Area

"Equation-Free" Simulation Methods for Multiple Timescale Diffusion Processes in Solids
130732

Year 3 of 3
Principal Investigator: G. J. Wagner

Project Purpose:
Many important and hard-to-solve problems related to the synthesis, performance, and aging of materials involve diffusion through the material or along surfaces and interfaces. Since accurate interatomic potentials exist to describe many materials at the atomic scale, these problems would seem to be candidates for modeling via molecular dynamics (MD) simulation. However, MD requires integration of timescales on the order of atomic vibrations (picoseconds), while many processes of interest in solids, including surface or bulk diffusion, occur on much longer timescales. This scale discrepancy renders MD simulation of many of these important problems intractable. A number of simulation methods have been put forward to remedy this difficulty. Notable among these are kinetic Monte Carlo (KMC) and temperature-accelerated dynamics (TAD), both of which follow individual events on the atomic scale (e.g., atom hopping) that drive the evolution of the material. Unfortunately, these methods have their own limitations on attainable timescales and number of atoms in the simulation. To make further progress, we can note that the quantities most of interest to a modeler, such as concentrations and structural feature sizes, can be described at a much coarser level than the atomic scale. One method that takes advantage of this fact is the so-called "equation-free" approach, which uses microscale computations as a set of numerical experiments from which can be distilled macroscale information, such as time derivatives of coarse scale variables. We are using equation-free methods to extend atomistic simulations to the timescales necessary for accurate simulation of diffusion processes. The key innovation in our project is the use of extended timescale atomistic methods, like KMC and TAD, for the fine-scale computations that inform the continuum-level evolution in an equation-free approach. A successful project will result in a capability at Sandia for simulating synthesis and aging processes that currently can only be explored through experimentation.

Summary of Accomplishments:
The results of our project can be summarized in four major areas of achievement:

- We have added parallelized implementations of accelerated MD methods to the large-scale atomic/molecular massively parallel simulator (LAMMPS) code. In particular, the parallel replica dynamics (PRD) and TAD methods have been implemented, along with nudged elastic band (NEB), a method for computing activation energies between states. Innovations have been made in the parallelization of these schemes.
- We have demonstrated the use of the equation-free projective integration (EFPI) method for accelerated simulations of solid surface evolution. This is the first application of the method to the evolution of solid surface profiles, a phenomenon that is extremely important in understanding the aging of nanostructured materials. Simulation speed-ups of 20 times have been demonstrated, with the possibility of further improvement. As part of our research, we have shed light on the types of coarse variables that must be used to parameterize the slow dynamics of evolving solid systems.
- We have developed a new, generalized method for initializing fine-scale systems based on the principle of maximum entropy. This work was motivated by previous difficulties generating systems that are consistent with a given coarse-scale description, but also obey the proper dynamics in time.

The method that we have developed allows all but the slowest coarse-scale variables to come into equilibrium; we have shown that properly doing this allows us to reproduce the correct dynamics of the system.

- We have developed new interscale operators for bulk diffusion processes and implemented them in LAMMPS. These operators can be used to distill a set of atomic positions into a spatially varying continuum concentration field (the "restrict" operation), and in the other direction, to randomly generate a set of atomic positions consistent with a given continuum concentration field (the "lift"" operation).

Significance:
The accomplishments of our project will impact Sandia's ability to perform atomic scale simulation of material stability and nanoscale transport over long times, phenomena that are vital to modeling aging of the nuclear stockpile and the design and development of new materials for nuclear weapons (NW) and energy applications. Some of the applications of our results will be immediate, while others will take place over the long term as our methods are further developed and integrated into materials simulation research.

The new accelerated MD methods added to the LAMMPS code will impact a range of research projects in the design and analysis of complex materials, including NW and energy applications. By including these methods in the LAMMPS software release, we have made them available throughout Sandia as well as to the external research community. These tools are available now and will be put to use in ongoing multiscale material modeling projects. Likewise, the interscale operators for bulk diffusion processes that we have developed are available now in Sandia research codes and will have immediate effect on S&T through their utilization on current projects.

Our work on developing the EFPI method for diffusion problems, including our new maximum entropy method, will have an impact over the longer term as we refine the algorithm for specific applications related to both NW and energy materials. In addition, the maximum entropy method we have developed has use not just in our EFPI algorithm but in molecular dynamics, atomistic-to-continuum, and any method in which it is useful to generate the fine-scale representation of a system based on a coarse-scale description. With further development this has potential to affect a wide range of S&T, NW, and energy materials problems.

Bayesian Data Assimilation for Stochastic Multiscale Models of Transport in Porous Media
130734

Year 3 of 3
Principal Investigator: J. Ray

Project Purpose:
Our research is focused on developing new Bayesian inference methodologies that characterize coupling across multiple spatiotemporal scales and heterogeneous physical processes by conditioning on observational data. Our techniques are general, but will be demonstrated on problems in porous media. Multiphase transport in porous media underpins applications of great importance to energy and the environment (e.g., fuel cells, subsurface nuclear waste storage, CO_2 sequestration). These physical processes are inherently multiscale, driven by pore-scale characteristics such as capillarity, relative permeability, and reactivity. A fundamental difficulty in multiscale modeling is indeterminacy in extrapolating from microscale simulations to macroscale characteristics, and conversely, the inability of a macroscale model to resolve inputs needed at the microscale. Traditional upscaling/homogenization techniques ignore or arbitrarily simplify these uncertainties, failing to reproduce measured processes at multiple scales. Crucial statistical information and opportunities to provide validated predictions is, therefore, lost. We address these shortcomings by developing statistical inversion algorithms that infer the correct interscale coupling by conditioning on observables. Our algorithms will provide macroscale properties with quantified uncertainties, using spectral representations of multiscale random fields. Novel reduced-order representations of state variables and joint uncertainties at multiple scales will preserve computational tractability. The data-driven methods developed here will enable rigorous updating and refinement of computational characterizations and forecasts in conjunction with experimental observations.

The project brings together developments over the last five years in multiscale finite-element methods, random field models, and parallel Markov Chain Monte Carlo samplers to address a challenging problem in stochastic upscaling. Many of the underlying assumptions have been proved only in allied fields and never in an integrated manner on a multiscale problem. The project is, therefore, risky and much about the accuracy, robustness, and scalability of the numerical methods planned in this project remain topics of investigation.

Summary of Accomplishments:
The main accomplishment of this project, over its three years, was to extend our Bayesian inference capabilities to include multiscale random fields. It laid the modeling and algorithmic groundwork for their use in diverse inverse problems. We demonstrated our capabilities on the estimation of permeability fields from sparse observations of permeability and transport through the medium.

Random fields are typically defined on a grid; “multiscale” refers to structures resolved by it. A novel aspect of multiscale inference that we addressed was the estimation of structures too small to be resolved on a grid. This required the establishment of an interscale link function. We used truncated Gaussians to create a parameterized representation of subgrid structures (in particular, inclusions in a binary medium) and employed it to develop an upscaling relation for permeability. We solved a Bayesian inverse problem to reconstruct the spatially variable inclusion proportion and inclusion size of the binary medium. A Karhunen-Loeve (KL) expansion of a multiGaussian field was used to reduce the dimensionality of the inverse problem. An adaptive Markov chain Monte Carlo method was used to sample the posterior distribution of the KL weights. We identified the information content of various kinds of observations. We then addressed the case where an explicit subgrid model was not available, and used multiscale finite elements to provide the interscale relationship instead.

We also developed ensemble Kalman filters (EnKF) to perform inversions scalably. EnKFs typically assimilate only time-variant observations, and we adapted them so that static observations could also be included. They were tested on reconstruction problems, where the permeability field resembled those of fluvial beds. Finally, we subjected the EnKF to a highly nonlinear problem (i.e., that of estimating the conductivity field of a corner of the Ogallala aquifer) using a transport model developed by the Kansas Geological Survey.

The key accomplishments of this project are: 1) development of MCMC samplers, 2) development of EnKF based technology for inference problems, 3) experience with varied random field models, 4) experience with, and demonstration of, the use of Karhunen-Loeve expansions in large, inferential problems, and 5) development of statistical subgrid models to represent unresolved physics/structures and their use in inverse problems.

Significance:
Subgrid models are being investigated, for CO_2 sequestration reservoirs, in an Energy Frontier Research Center. Multiscale random field models formed part of a successful Advanced Scientific Computing Research proposal on matrix completion techniques and a successful LDRD project focused on estimating multiresolution random fields under sparsity priors. Finally, EnKFs developed in this project are being used in other LDRD projects targeting the estimation of anthropogenic CO_2 emissions from sparse observations.

The capabilities developed by this project can be used in a number of other problems. The project's porous media aspect connects it directly to DOE's ongoing research efforts in CO_2 sequestration elsewhere, environmental remediation of DNAPL-contaminated sites, and transport-reaction coupling in fuel cells. This project is also consistent with Sandia's DoD mission space in areas of transport and decontamination of chemical weapon agents and toxic industrial chemicals in porous/construction media. Inference techniques developed in this project will also apply to other matrix completion problems, for example, those encountered when constructing the adjacency matrix of networks from sparse observations (network tomography).

Refereed Communications:
S.A. McKenna, J. Ray, Y. Marzouk, and B. van Bloemen Waanders, "Truncated MultiGaussian Fields and Effective Conductance of Binary Media," *Advances in Water Resources*, vol. 34, pp. 617-626, May 2011.

Computational Mechanics for Geosystems Management to Support the Energy and Natural Resources Mission
130739

Year 3 of 3
Principal Investigator: M. J. Martínez

Project Purpose:
The main objective of this project was to enable a foundational capability for advanced modeling of coupled multiphysics subsurface processes. US energy needs include more economical extraction of fossil fuels, increasing recoverable reserves, protection of water resources, reduction of the impact of fossil fuels on climate change, mining nuclear fuel sources with minimal environmental impact, and technologies for safe disposal of energy wastes. In addition, this research supports many crucial Sandia projects: geologic sequestration of CO_2 (a National Academy of Engineering challenge problem), thermochemistry/decomposition of porous high explosive, encapsulant foams and ablative materials, advanced designs of thermal/flow batteries, and many other projects in energy security. Long-term solutions to these needs require the ability to model and predict behavior of subsurface systems including complex, heterogeneous porous rock thermal-chemical-mechanical behavior as well as the interactions with pore fluids. This project will enable a coupled thermal, hydrological, mechanical, chemical (THMC) simulation capability for massively parallel applications. Key research issues addressed are related to thermodynamic phase behavior of complex fluid mixtures, geologic heterogeneity and other subgrid phenomena, robust solvers for fully coupled (especially chemically reactive) systems, and methods to deal with disparate time and length scales for the coupled multiphysics. To solve these complex issues, this project integrated research in numerical mathematics and algorithms for chemically reactive multiphase systems with computer science research in adaptive coupled solution control and framework architecture.

Summary of Accomplishments:
The main accomplishment was the development of a foundational capability for coupled THMC simulation of heterogeneous geosystems utilizing massively parallel processing. The following lists key accomplishments from this project:

- General capability for modeling nonisothermal, multiphase, multicomponent flow in heterogeneous porous geologic materials.
- General capability to model multiphase reactive transport of species in heterogeneous porous media.
- Constitutive models for describing real, general geomaterials under multiphase conditions utilizing laboratory data.
- General capability to couple nonisothermal reactive flows with geomechanics THMC.
- Phase behavior thermodynamics for the CO_2-H_2O-NaCl system. General implementation enables modeling of other fluid mixtures. Adaptive look-up tables enable thermodynamic capability to other simulators.
- Capability for statistical modeling of heterogeneity in geologic materials.
- Simulator utilizing unstructured grids on parallel processing computers.

Significance:
The accomplishments of this project align very well with DOE and Sandia's strategic goals of energy, science and the environment. This project allows Sandia to address many of the issues associated with protecting our economic and national security by assisting in the development of a diverse energy portfolio while improving the quality of the environment. The project end state places Sandia and DOE

in a favorable position to address the wide range of multiphysics and multiscale issues associated with the entire energy cycle from in situ fuel extraction to waste disposal.

Refereed Communications:

S.M. Davison, H. Yoon, and M.J. Martínez, "Pore Scale Analysis of the Impact of Mixing-Induced Reaction on Viscosity Variations," *Advances in Water Resources*, vol. 38, pp. 70-80, March 2011.

D.Z. Turner, K.B. Nakshatrala, M.J. Martínez, and P.K. Notz, "Modeling Subsurface Water Resource Systems Involving Heterogeneous Porous Media Using the Variational Multiscale Formulation," to be published in the *Journal of Hydrology*.

C.M. Stone, M.J. Martínez, J.F. Holland, T. Dewers, F. Hansen, E. Hardin and J. Argüello, "Coupled Thermal-Hydrological-Mechanical-Chemical Analyses of a Repository in Clay/Shale for High-Level Waste," in the *Proceedings of the American Rock Mechanics Association (ARMA), 45th US Rock Mechanics and Geomechanics Symposium,* June 2011.

K.B. Nakshatrala and D.Z. Turner, "A Mixed Formulation for a Modification to Darcy Equation with Applications to Enhanced Oil Recovery and Carbon-Dioxide Sequestration," to be published in the *Journal for Computational Methods in Engineering Science and Mechanics*.

Experimental Characterization of Energetic Material Dynamics for Multiphase Blast Simulation
130740

Year 3 of 3
Principal Investigator: S. J. Beresh

Project Purpose:
Accurate simulation of energetic material detonation is crucial to a variety of national interests involving explosive devices, including vulnerability of weapons and structures to nearby explosions, blast mitigation, improvised explosive device (IED) protection, and enhanced blasts. Unfortunately, such predictive capability is limited by a lack of knowledge of the underlying phenomena of the earliest stages of the blast, where the particle dynamics of the fragmented materials within the gas expansion products are pivotal to understanding the continuing reaction. The complication is that, at the explosion's onset, the particles are densely packed within the expanding flow, whereas our knowledge of the process is restricted to dilute concentrations. One of the great challenges of this problem is that the opacity of the flow due to the large particle density prevents usage of common fluid dynamics diagnostics and instead will require the development of unconventional measurement approaches.

We are filling this knowledge gap by constructing an unprecedented multiphase shock tube that can drive a shock front into a particle/gas mixture of a selected fill fraction, then measure the motion of the densely packed particles within the expanding gas. To penetrate the dense flow and provide measurement of the particle velocities, we seek to exploit measurement concepts previously utilized for multiphase flows and high-energy physics and adapt them to the uncommon difficulties of the present problem. No such experimental technology presently exists. The most promising approaches use x-ray sources, or potentially strong incoherent visible light, in concert with specifically designed tracer particles. Finally, while velocity measurements are of the greatest value, the lack of knowledge of this flowfield is so profound that even delivery of simpler measurements such as shock speeds and pressure histories would represent a valuable contribution. By providing crucial new physical data, we can boost the level of fidelity in algorithms used to simulate blasts in national security applications.

Summary of Accomplishments:
To address the lack of data for interactions of shock waves with particle fields between the dilute and granular regimes, a novel multiphase shock tube (MST) has been constructed to drive a planar shock wave into a dense gas-solid field of particles. A nearly spatially isotropic field of particles is generated in the test section by a gravity-fed method that results in a spanwise curtain of spherical 100-micron particles having a volume fraction of about 19%. Interactions with incident shock Mach numbers of 1.66, 1.92, and 2.02 were achieved. High-speed schlieren imaging simultaneous with high-frequency wall pressure measurements are used to reveal the complex wave structure associated with the interaction. Following incident shock impingement, transmitted and reflected shocks are observed, which leads to differences in particle drag across the streamwise dimension of the curtain. Shortly thereafter, the particle field begins to propagate downstream and spread. For all three Mach numbers tested, energy and momentum fluxes in the induced flow far downstream are reduced about 30-40% by the presence of the particle field. X-ray diagnostics have been developed to penetrate the opacity of the flow, revealing the concentrations throughout the particle field as it expands and spreads downstream with time. Furthermore, an x-ray particle tracking velocimetry diagnostic has been demonstrated to be feasible for this flow, which can be used to follow the trajectory of tracer particles seeded into the curtain. Additional experiments on single spherical particles accelerated behind an incident shock wave have shown that elevated particle drag coefficients can be attributed to increased compressibility rather

than flow unsteadiness, clarifying confusing results from the historical database of shock tube experiments. The development of the Multiphase Shock Tube (MST) and associated diagnostic capabilities offers experimental capability to a previously inaccessible regime that can provide unprecedented data concerning particle dynamics of dense gas-solid flows.

Significance:

A consequential improvement to blast simulation is unlikely to occur without improvement in the understanding of the underlying reaction physics, which would benefit core Sandia responsibilities regarding vulnerability of weapons and structures to nearby explosions, facilities protection, explosive design, and blast mitigation, as well as nuclear weapon applications. Furthermore, given Sandia's involvement in other research initiatives covering such explosive topics as enhanced blasts, structure-coupled blasts, improvised explosive device protection, and thermobaric explosives, an infusion of new data is of direct and wide-ranging programmatic importance. Thus, the present research effort is of great interest to Sandia's defense programs, and additionally to the broader national defense establishment.

The present research program is specifically designed to return unprecedented data concerning the reaction regime immediately following detonation. This has provided new physical understanding unavailable anywhere else, which then will influence the development of computational models for blast simulation. In fact, some of our experiments have resulted in revised physical understanding of previously published data by established researchers. Numerous technical publications describing such new achievements have been published in the final year of this program, with more expected beyond the end of this project, as we publicize our final successes.

These new testing capabilities are unique for the national explosives research community, offering experimental capability to a previously inaccessible regime. Since the accurate simulation of energetic material detonation is crucial to a variety of national interests involving explosive devices, many future experiments are planned utilizing the new capabilities developed under this program. To gain the physical understanding necessary for high-fidelity modeling requires moving from low-fidelity explosive field tests to scientifically controlled experiments. To accomplish this task, our unique MST will be utilized to provide a wide range of physical data concerning the particle dynamics of dense gas-solid flows. No such data presently exist, except those acquired under the current project as new capability was developed. New results would have an immediate impact upon the modeling and simulation of energetic materials. The value of the new capability and the proposed follow-on work has been recognized by multiple funding programs within DOE and DoD.

Refereed Communications:

J.L. Wagner, S.J. Beresh, S.P. Kearney, W.M. Trott, J.N. Castañeda, B.O. Pruett, and M.R. Baer, "A Multiphase Shock Tube for Shock Wave Interactions with Dense Particle Fields," to be published in *Experiments in Fluids*.

J.L. Wagner, S.J. Beresh, S.P. Kearney, W.M. Trott, J.N. Castañeda, B.O. Pruett, and M.R. Baer, "Interaction of Planar Shock with a Dense Field of Particles," in *Proceedings of the 17th Meeting of the American Physical Society Shock Compression of Condensed Matter,* June 2011.

J.L. Wagner, S.J. Beresh, S.P. Kearney, W.M. Trott, J.N. Castañeda, B.O. Pruett, and M.R. Baer, "Interaction of a Planar Shock with a Dense Field of Particles," in *Proceedings of the 28th International Symposium on Shock Waves,* July 2011.

Nanomanufacturing: Nanostructured Materials Made Layer-by-Layer
130741

Year 3 of 3
Principal Investigator: P. R. Schunk

Project Purpose:
Large-scale, high-throughput production of nanostructured materials (i.e., nanomanufacturing) is crucial to national security and a strategic area in manufacturing, with markets projected to exceed $1T by 2015. Nanomanufacturing is still in its infancy; process/product developments are costly and only touch on potential opportunities enabled by growing nanoscience discoveries. Interestingly, the greatest promise for high-volume manufacturing lies in age-old coating and imprinting operations. For materials with tailored nanometer-scale structure, imprinting/embossing must be achieved at high speeds (roll-to-roll) and/or over large areas (batch operation) with feature sizes less than 100 nm. Dispersion coatings with nanoparticles (NPs) can also tailor structure through self or directed assembly. Layering films structured with these processes has tremendous potential for efficient manufacturing of microelectronics, photovoltaics, and other nanostructured materials. This project is aimed at expediting benchtop to manufacturing scaleup through modeling and simulation (M/S); project success is critical for broadening Sandia's advanced simulation and computing (ASC)-class software for impact in nanoengineering. Connecting machine design variables to design parameters (e.g., feature size/structure) is challenging due to a large range of relevant length/time scales. Computational models of coating and imprinting operations have been invaluable to manufacturing; application to nanomanufacturing is topical, uncharted, and ripe for scientific breakthroughs. During the entirety of this project, research and development has led to innovations in finite-element technology, subgrid physics models, experimental discoveries, and unprecedented multiscale analysis, leading to heightened interest and even additional funds from private industry. In the final year, we also achieved our first level of validation for several of our models.

Summary of Accomplishments:
Successful outcomes in this project are numerous. We list here those which we feel can serve as technology base for current and future customers. In all cases, the final capabilities were completed in FY 2011.

- Production computing capability for applying effective traction-separation laws for adhesive de-bonding of structured rough surfaces (in SIERRA application PRESTO).
- Production computing capability for thin-film, thin-gap, thin-porous regions in a generalized shell-element format (in finite element code GOMA).
- Production capability for modeling the dynamics of polymer-grafted nanoparticles with general polydispersity (in production code large-scale atomic/molecular massively parallel simulator [LAMMPS]).
- Pixel-to-mesh image mapping capability (GOMA).
- Coupled thin-shell lubrication and thin-porous shells with continuum finite element regions of arbitrary physics (GOMA).
- Established capability and workflow for nanomanufacturing processes involving imprint, emboss-and-release unit operations with arbitrary feature patterns. Validated imprinting capabilities with experimental data from Molecular Imprints Inc.
- Established capability and workflow for modeling the directed assembly of nanoparticles at the meso- and continuum scale.

Significance:
Breakthrough technologies for safe, affordable, abundant energy require volume production. Whether it is photovoltaic, thermoelectric, or photosynthesis technology, nanotechnology discoveries are stymied by lack of viable manufacturing approaches. This project expands Sandia and DOE’s existing nanotechnology thrusts in these areas into the manufacturing sector and increases the return on investment in nanoscience; current DOE programs are not addressing manufacturing, to our knowledge. This is the only effort to bridge our plethora of nanoscience activities in S&T to the manufacturing sector, and hence, is crucial to US competitiveness. Several derived benefits to S&T community have already been realized, including impact on Work for Others problems.

Refereed Communications:
H. Wu, F. Bai, Z. Sun, R.E. Haddad, D.M. Boye, Z. Wang, and H. Fan, “Pressure-Driven Assembly of Spherical Nanoparticles and Formation of 1D-Nanostructure Arrays,” *Angewandte Chemie International Edition*, vol. 49, pp. 8431-8434, November 2010.

E.D. Reedy, Jr. and J.V. Cox, “Hierarchical Analysis of Nano-Imprint Release Using an Adhesion/Atomistic Friction Surface Interaction Model,” to be published in the *Journal of Applied Mechanics*.

S. Xiong, R. Molecke, M. Bosch, P.R. Schunk, and C.J. Brinker, "Transformation of a Close-Packed Au Nanoparticle/Polymer Monolayer into a Large Area Array of Oriented Au Nanorods via E-Beam Promoted Uniaxial Deformation and Room Temperature Sintering,” *Journal of the American Chemical Society*, vol. 133, pp. 11410-11413, June 2011.

Optimization of Large-Scale Heterogeneous System-of-Systems Models
130742

Year 3 of 3
Principal Investigator: J. D. Siirola

Project Purpose:
Decision-makers increasingly rely on large-scale computational models to simulate and analyze complex man-made systems. For example, computational models of national infrastructures are being used to inform government policy, assess economic and national security risks, evaluate infrastructure interdependencies, and plan for the growth and evolution of infrastructure capabilities. A major challenge for decision-makers is the analysis of national-scale models that are composed of interacting systems: effective integration of system models is difficult; there are many parameters to analyze in these systems, and fundamental modeling uncertainties complicate analysis. The purpose of this project is to develop optimization methods for effectively analyzing large-scale heterogeneous system of systems (HSoS) models, which have emerged as a promising approach for describing such complex man-made systems. These optimization methods will enable decision-makers to predict future system behavior, manage system risk, assess trade-offs among system criteria, and identify critical modeling uncertainties.

Optimization is a promising strategy for analyzing HSoS models because it can be tailored to address a decision-maker's analysis question. HSoS applications share several features that motivate the optimization research in this project: 1) there is fundamental uncertainty in the data, which comes from a diverse range of sources, 2) HSoS models often describe how systems evolve over time, and 3) there are many criteria for assessing the performance of HSoS systems. This project is integrating the following research areas to provide a comprehensive capability for analyzing complex, large-scale HSoS models:

- Multi-stage stochastic optimization with recourse will be used to plan and manage system evolution through time, given uncertain information about the future.
- Risk management will be used to identify system parameters that are insensitive to data uncertainties.
- Multi-objective optimization techniques will assess tradeoffs among HSoS performance criteria, including risk, cost, and system performance.
- Model reduction and surrogate methods to provide efficient approximations of HSoS systems with discrete components.

Summary of Accomplishments:
- We developed a general progressive hedging (PH) solver in PySP (Python-based Stochastic Programming) to support minimization of the conditional value at risk measure, compute confidence intervals on the value of final solution implemented scenario clustering to speed convergence; we devised a generic infrastructure for parallelizing PH on clusters and massively parallel computers, and included a linearization of the quadratic equations used by PH.
- We applied PH to large-scale multistage resource allocation, sensor placement, and nonlinear parameter estimation problems. We collaborated with researchers at Lawrence Livermore National Laboratory on a test case using a nuclear weapons-related enterprise planning application.
- We identified and evaluated candidate mixed-variable surrogate modeling approaches and prototype implementations, and we identified possible roles for surrogates in mixed-integer and/or stochastic programming algorithms.

- We developed a fundamental new approach to optimization "middleware" through the COLIN optimization interface library, providing an extensible framework for hybrid and multimodel optimization, with particular focus on multi-objective and nondeterministic problems.
- We developed collaborations with academic groups at the University of California, Davis, Universidad de Chile, Iowa State University, North Carolina State University, Rose-Hulman University, and Texas A&M University to use the Coopr (computational infrastructure for operations research) software we developed in a variety of optimization applications and classroom environments. We have also integrated Coopr into the Computational Infrastructure for Operations Research (COIN-OR) project, an initiative to spur the development of open-source software for the operations research community.
- Over three years, project members gave 37 presentations at international conferences, including one keynote address. We also published two conference papers and three journal articles. We distributed research results through 28 software releases. There have been over 12,000 unique downloads and checkouts of software packages developed and supported by this project.

Significance:
Many Sandia, DOE, and DoD programmatic thrusts concern the analysis of complex man-made systems, and computational models of these systems are increasingly used to assist decision-makers and inform national policy. For example, Sen. Jeff Bingaman (D-NM) recently noted that "robust models of our energy use . . . can help the raise technical level of our policy discussions in Washington."

Refereed Communications:
J.-P. Watson and D.L. Woodruff, "Progressive Hedging Innovations for a Class of Stochastic Mixed-Integer Resource Allocation Problems," *Computational Management Science*, vol. 8, pp. 355-370, 2011.

W.E. Hart, J.-P. Watson, and D.L. Woodruff, "Pyomo: Modeling and Solving Mathematical Programs in Python," *Mathematical Programming Computation*, vol. 3, pp. 219-260, 2011.

System-Directed Resilience for Exascale Platforms
130743

Year 3 of 3
Principal Investigator: K. B. Ferreira

Project Purpose:
Resilience on massively parallel processing (MPP) systems has traditionally been the responsibility of the application, with the primary tool being application-directed checkpoints. However, as systems continue to increase in size and complexity, the viability of application-directed checkpoint as a solution decreases. Recent studies performed at Sandia projected that as systems grow beyond 100,000 components, a combination of factors lead to checkpoint overheads in excess of 50%. In this project, we are investigating critical changes required in MPP systems software to support system-directed resilience. The goal is to provide efficient, application-transparent resilience through coordinated use of system resources. The primary research topics focus around the problem of continuous computing in the event of a component failure. A preliminary list of required new capabilities includes the following:

- Application Quiescence: the ability to suspend central processing unit (CPU), network, and storage services used by an individual application without interfering with the progress of other applications
- State Management: the ability to identify, extract, and manage application state in a transparent, efficient, and non-intrusive way
- Fault Recovery: the ability to transparently replace a failed component without restarting the entire application

Many other researchers in the field and the manufacturers of large-scale systems are aware of the looming problem and these teams are pursuing many different approaches. Most likely, a combination of technologies and approaches is needed to find a satisfactory solution. This is especially the case in light of new architectural features, such as compute accelerators and a large increase in the number of cores and complexity in CPUs. The lack of experience in using these new technologies, the unknown of what architectural features will prevail, and the extreme scale of these future machines make research in this area very difficult and the outcome extremely uncertain.

Summary of Accomplishments:
A good portion of our efforts and time this year went toward a formalized understanding of our state-machine replication approach for exascale-class systems. Using a combination of modeling, empirical analysis, and simulation, we studied the costs and benefits of this approach in comparison to checkpoint/restart on a wide range of system parameters. These results, which cover different failure distributions, hardware mean time to failures, and input/output (I/O) bandwidths, show that state machine replication is a potentially useful technique for meeting the fault tolerance demands of high performance computing (HPC) applications on future exascale platforms. A paper accepted to this year's annual supercomputing conference has generated considerable interest within the HPC community. This has resulted in collaborations with National Center for Supercomputing Applications (NCSA), IBM, and Los Alamos National Laboratory (LANL), all currently in formative stages. These will supplement established collaborations currently in place with North Carolina State University (NCSU), the University of New Mexico (UNM), and Oak Ridge National Laboratory. Another output of this work is the release of the rMPI software library, which enables transparent replication for message passing library (MPI)-based applications. Work with NCSU and UNM is ongoing to further enhance this resilience library.

A portion of our efforts this year were invested in refining our memory characterization work, as well as exploring the role new architectural features —such as graphic processing units (GPU) and multicore processors — play in creating and managing checkpoints. To this end, we created Libhashckpt, a system-level incremental checkpointing library that utilizes GPUs to dramatically reduce checkpoint overhead.

Lastly, through this study, we have been able to evaluate the limits of a systems-level approach to application fault tolerance. The evaluation of this limit has shown the importance and need of incorporating resilience directly into the operating system and runtime. This discovery has led to a new LDRD project.

Significance:
This project has direct relevance to Sandia's science, technology, and engineering missions. The important lessons learned from this work can have direct impact on applications in virtually all areas of advanced computing throughout the DOE complex. A key aspect of this work is that our approach represents a fundamental change in the way MPP systems support resilience — shifting the view from failures as a rare event that applications can directly handle, to a view of failures as a relatively commonplace event that can be more effectively handled by the system with minimal application modification. Therefore, this approach significantly reduces the burden of resilience on the application developer, simplifying the development process for the scientist. Additionally, this effort can have a significant impact on performance and resource utilization by reducing, in some cases by orders of magnitude, the network and storage requirements for fault tolerance on large-scale systems.

An Internet Emulation System to Enable Predictive Simulation of Nation-Scale Internet Behavior
141505

Year 2 of 3
Principal Investigator: R. G. Minnich

Project Purpose:
We are constructing an emulation platform that will allow us to model, analyze, and predict the behavior of nation-scale networks — i.e., networks of one to ten million machines. The millions of machines will be started up in less than five minutes. The system of millions of machines will be self-organizing, as the Internet is, with a minimal set of configuration files and parameters. The system will have a system that parallels the real Internet, with domain name service servers, border gateway protocol nodes, and other services as needed. The system will allow us to vary details of network protocols and other parameters and explore the impact on the operations of large Internet Protocol (IP) networks. Additional software will include data collection, analysis, and visualization tools to allow the non-expert to get a clear view of what is transpiring when an IP network (such as the Internet) is experiencing problems. Finally, we are developing techniques that can be used to protect real-world organizations such as the US government from Internet attacks.

Summary of Accomplishments:
This year, we stood up the KANE and Strongbox clusters. KANE is a 520-node Intel testbed connected via Gigabit Ethernet. We developed software that allowed us to boot 70,000 Windows virtual machines and 600,000 Linux virtual machines.

We continued to create new software that should allow us to continue to scale. An interesting fact is that in 2009, we needed 5000 nodes to run one million virtual machines. With the newest software we have created, we should be able to use 520 nodes to run 800,000 virtual machines. In two years, we have become an order of magnitude more effective.

Significance:
Our work will support Sandia's mission in cyber, including participation in the National Cyber Range. Our work will also resonates with the mission to protect the nation's critical infrastructures by assisting efforts to protect the Internet itself, as well as other critical infrastructures dependent on the Internet. Our project also undergirds Sandia's strategy articulated in response to the Comprehensive National Cyber Initiative by engaging in cyber threat analysis, by assisting the prototyping of sophisticated defensive systems, by furthering cyber science and technology research and development, and by supporting policy formulation.

Effects of Morphology on Ion Transport in Ionomers for Energy Storage
141506

Year 2 of 3
Principal Investigator: A. Frischknecht

Project Purpose:
Polymer electrolytes are essential elements of current and next-generation energy storage applications. An important class of polymer electrolytes is ionomers, in which one of the ions is covalently bound to the polymer backbone. Ionomers are currently used in fuel cells, and show extraordinary promise as solid electrolytes in batteries for transportation and portable-power applications. Solid electrolytes are desirable for a variety of reasons. A primary one is safety: the lack of solvent leads to fewer electrochemical reactions (e.g., with the electrodes) and the absence of flammable liquids. Solvent-free electrolytes allow for less packaging (and hence higher energy density batteries) and easier manufacture. Single-ion conductors such as ionomers also have the advantage of higher efficiency (high lithium transference numbers), since the anions are bound to the polymer backbone and the current is primarily due to the cations that actively participate in the electrochemical reactions. However, to date ionomeric materials do not have sufficiently high conductivities. Ion transport mechanisms in ionomers and their relation to molecular structure are poorly understood, although it is known that ion transport is coupled to polymeric motion and to the nanoscale morphology of ionic aggregates that often self-assemble in the polymer matrix. We are developing and using a suite of multiscale models and tools to investigate the structure of ionic groups and aggregates in ionomers, and to predict their effects on ion transport. The ability to predictively model these materials will enable the design and synthesis of new ionomers, which could lead to sizeable improvements in battery safety and performance essential for electrified vehicles.

Summary of Accomplishments:
Our work to date has mostly focused on method development and on understanding the structure and morphology of ionic aggregates in ionomers. We performed a large set of coarse-grained (CG) molecular dynamics (MD) simulations of ionomer melts with two different architectures. Regularly spaced charged beads were placed either in the polymer backbone (ionenes) or pendant to it. We found that the ionomers with pendant ions formed compact, discrete aggregates with liquid-like interaggregate order. This is in qualitative contrast to the ionenes, which formed extended aggregates. We have begun atomistic MD simulations of poly(ethylene-co-acrylic acid) (PE-AA)-based ionomers, both in the acid form and neutralized with Li ions. Ion diffusion is very slow in these systems, requiring long simulation times. The scattering structure factor from both CG and atomistic simulations is in good agreement with x-ray scattering data. We completed ab initio studies of the solvation of Li^+ in water. We have performed quantum density functional theory (DFT) calculations of structures and energies of ions (Li, Na, Cs, and Zn) interacting with acetate molecules (to mimic a fragment of the ionomer) in the gas phase and will next add solvent and then compare with experiment. The PE-AA ionomers have been characterized with solid-state ^{1}H, ^{13}C, and ^{7}Li NMR. We found the acid form of the polymer forms strong dimers, while details of molecular architecture and neutralization level affect the morphology of amorphous and crystalline regions. Finally, in our fluids-DFT code, the solver for charged polymeric systems was much improved, enabling future fluids-DFT calculations of ionomer phase behavior.

Significance:
Better electrical energy storage is crucial to the energy future of the nation along with supporting improved national security. DOE has identified fundamental research into new materials and technologies as essential to achieving this goal. This project contributes to DOE's mission in energy

storage by enabling predictive simulation of a potentially revolutionary new ionomer electrolyte. The success of this project would enable the design of better ionomers for lithium ion batteries, leading to safer and more efficient batteries with higher energy density for vehicle transportation and portable power applications.

Refereed Communications:

L.M. Hall, M.J. Stevens, and A.L. Frischknecht, "Effect of Polymer Architecture and Ionic Aggregation on the Scattering Peak in Model Ionomers," *Physical Review Letters*, vol. 106, p. 127801, March 2011.

T.M. Alam, D. Hart, and S.L. Rempe, "Computing the ^{7}Li NMR Chemical Shielding of Hydrated Li^{+} using Cluster Calculations and Time-Averaged Configurations from *ab initio* Molecular Dynamics Simulations," *Physical Chemistry Chemical Physics*, vol. 13, pp. 13629-13637, June 2011.

Multiscale Models of Nuclear Waste Reprocessing: From the Mesoscale to the Plant Scale
141508

Year 2 of 3
Principal Investigator: R. R. Rao

Project Purpose:
Nuclear waste reprocessing and nonproliferation models are needed to support the renaissance in nuclear energy, a proven technology without a carbon footprint. Our aim is to develop predictive capabilities targeting the design and monitoring of a next-generation nuclear fuel cycle to enable economic large-scale reprocessing with accurate material balances to mitigate public concerns regarding waste disposal and proliferation. Pu/U extraction models are being developed in SIERRA Mechanics at the droplet and contactor-scales, using a conformal decomposition finite element method (CDFEM) representation of the interfacial mass transport that occurs in the turbulent emulsion. Mass transport will be predicted using Cantera thermodynamics. Radionuclide distributions will be used in SCEPTRE to determine criticality and contactor size. Column-scale models are being developed to investigate placements and coupling. Plant flow sheets are being created using a novel, scalable network model that will allow coupling of massively parallel contactor models to simple models for other plant unit operations. This will be critical to support nonproliferation activities including material accountancy, plant design, and diversion scenarios. Models will be validated through experiments at Sandia and Oak Ridge National Laboratory.

This work is leveraging expertise in turbulent reacting flow, concentrated-solution thermodynamics, level set technology, neutronics, network modeling, and uncertainty qualification by coupling and extending them to address separations. Though we focus on reprocessing, the development is applicable to problems in the energy and weapons sectors, from refineries to ethanol production and radionuclide separations. Separations modeling, implicit to the chemical and oil industries, is still rudimentary and has not seen the benefits of high-performance computing. Flow sheets, critical to design and troubleshooting of plants, also have not taken advantage of the advances in parallel, modern, architectures, and numerical methods. We are developing advanced capabilities to simulate plants and separations using our expertise in developing engineering models of complex systems, experiments of discovery/validation, and high-performance computing. Models will advance the state-of-the-art at four length scales: droplet, contactor, column, and plant.

Summary of Accomplishments:
The emphasis for this year was to get the conformal decomposition finite element method (CDFEM) algorithm working for dynamics systems such as sheared and buoyant drops. This work will be the basis of the multidrop simulations necessary for the full contactor. To this end, a droplet-scale model using CDFEM has been developed and verified on a published 2D benchmark problem. This work was presented at the Finite Element in Fluids Conference [FEF11, Munich, Germany, March, 2011] and included the new mass transport model.

An experimental model system was developed using Neodimium and xylenol orange, with a new spectrophotometer to give quantitative mass transport data for the validation study. A quantitative droplet-scale mass transport validation experiment using the spectrophotometer was completed. The experiment was compared to CDFEM simulations. Contactor-scale experiments have been completed on a model water/polydimethyl siloxane (PDMS) system to determine droplet size as a function of RPM and position.

Advanced thermodynamic models have been developed for uranium dissolved in nitric acid contacted to an organic solvent in the presence of tributyl phosphate surfactant. A reduced order model of droplet size evolution in the contactor has been developed based on population balance modeling.

Significance:
Sandia has pioneered the field of surety by designing technology-based safety and security systems for nuclear weapons, and extending surety to commercial nuclear facilities for the Nuclear Regulatory Commission. We are developing technologies to ensure surety of nuclear waste reprocessing facilities by drawing on our engineering and computational science expertise, 12 years of advanced simulation and computing (ASC) SIERRA Mechanics code development, and over 60 years of surety engineering. This work will support DOE missions for nuclear energy and nonproliferation, as well as renewable, carbon-free energy. Improvements to SIERRA Mechanics for turbulent multiphase flow will also support the nuclear weapons program directly.

Predictive Multiscale Modeling of Thermal Abuse in Transportation Batteries
141509

Year 2 of 3
Principal Investigator: R. P. Muller

Project Purpose:
Transition from fossil-fueled to electrified vehicles depends on developing economical, reliable batteries with high energy densities and long life. Safety, preventing premature or catastrophic failure, is of paramount importance in battery design. The largest gaps in our technical understanding of the safe operation of electrical energy storage devices involve the fundamental mechanisms, energetics, and inefficiencies of complex processes that occur during battery operation that can lead to thermal runaway: charge transfer, charge carrier and ion transport, both in the bulk and at various interfaces, and morphological and phase transitions associated with Li-ion transport between cathode and anode. We are developing a comprehensive predictive capability for thermal management and the onset of thermal runaway in transportation-based secondary Li-ion batteries, rooted in a first-principles description of the governing atomistic processes at the electrode-electrolyte interface, propagating chemical information through multiple scales to a continuum-scale description of thermal transport and failure capable of addressing a variety of operational and thermal excursion conditions. The development of such a comprehensive model will enable scientists and engineers to identify and address potential safety and stability issues of new battery designs prior to experimental realization. This development will constitute a unique capability, and will be of great significance within Sandia, for the DOE and DoD, and for its current and future commercial partners.

Accurate description of the processes that lead to thermal runaway involves the interaction of physical processes at a number of different physical length scales. This sort of multiscale modeling is itself a challenging research project. Moreover, the abusive conditions of battery operation represent among the most challenging issues in battery modeling.

Summary of Accomplishments:
During the second year of our three-year project, we have made significant progress toward meeting our overall project goals. Thermal abuse processes are closely linked with the breakdown of the solid electrolyte interphase (SEI) passivation layer that forms on the anode process. We have developed a chemical mechanism for the formation of the SEI layer, and are using this mechanism in our kinetic Monte Carlo and continuum-level models of SEI growth. By constructing a detailed model for SEI layer growth under normal conditions, we anticipate being able to understand the reverse processes at elevated temperatures. We have similarly made great strides in our combined electrode-electrolyte simulation model, and are now passing information between the quantum mechanical and the solvation programs, although we have not yet iterating to convergence.

Significance:
The project leverages Sandia's expertise in battery abuse to develop a valuable capability for modeling batteries that can be used by other DOE projects and automobile manufacturers.
Advances in rechargeable batteries are key to realization of the goal of vehicle electrification. Our program will build on Sandia's recognized strengths in battery safety and abuse experimentation to create a predictive modeling capability for safety of transportation batteries. In addition to the predictive capability for thermal abuse modeling, this capability can form the underpinnings of an optimization tool for battery performance, giving Sandia a foundation and a strong edge in developing new

collaborations. These strengths will be particularly valuable to Sandia with the national focus on renewable energy and green transportation.

Risk Assessment of Climate Systems for National Security
141510

Year 2 of 3
Principal Investigator: G. A. Backus

Project Purpose:
The US Executive branch, many members of Congress, and defense and intelligence communities recognize that climate change has considerable potential to create high-consequence security threats. They further recognize the gap between climate science and Sandia's engineering risk-based analyses needed to characterize the national security threat. National security issues arising from perceptions of climate change already produce geopolitical tensions within the Arctic, Russia, China, and Africa. From population migration, to the loss of economic viability, to the new access to critical resources, to the disruption of strategic supply chains, climate change produces destabilization hazards across countries. To understand geopolitical issues, we must understand the dynamics of regional climate change and its concomitant effects on human and state behavior. Moreover, we must understand and accommodate the inescapable uncertainty in physical and human behavioral modeling before we can assign any level of confidence (validation) to the results that analyses produce. This effort will extend our existing climate capabilities to perform regional analyses and a comprehensive characterization of potential security threats. We are identifying emergent and signpost phenomena of climate change, along with sensitivity fingerprints. We will couple climate change, hydrological, and socioeconomic analyses with new uncertainty quantification methods (adapted from Sandia's Advanced Scientific Computing [ASC] and new Office of Science [SC] work) for examining the high-consequence tails of the climate probability distributions that dominate the risks and impacts for societies and economies.

Our previous work established that the primary path of climate change risk follows a course from local hydrological impacts affecting the ability to maintain local economic activity. Interregional socioeconomic interactions then produce ripple-effect impacts on a global scale with geopolitical ramifications. Decision support systems to quantify and manage the associated risk thereby require multiscale and coupled analyses. Methods to measure and encapsulate the dynamic uncertainty for supporting risk-informed policymaking are nonexistent.

Summary of Accomplishments:
This year, we have adapted ASC Predictive Capability Maturity Model (PCMM) methods to climate change for assessing the level of confidence in climate-impact results. The quantified metrics for capability maturity should have wide applicability among simulations that have irreducible uncertainty. We now have the routine ability to run the coupled climate model using Sandia high-performance computing. We have completed the sensitivity analysis for the Create Local Models code. The analysis showed that increased vegetation has its largest impact on insulating the ground heat from returning to the atmosphere. Previous analyses assumed the vegetation albedo would increase the transfer of heat to the atmosphere. Furthermore, the model results are strongly dependent on a fixed water-table level and the absence of human water uses — both of which are critical to climate-impact analyses. Our Arctic "emergent condition" work suggests that once the Arctic Ocean becomes ice free, it will have a high probability of being ice-free every summer, thereafter. Added indications are that the winter ice will be a reduced impediment to ship travel and dramatically affect Naval and US Coast Guard operational requirements.

Our geopolitical simulations now include the complete macroeconomic data sets for 230 nations/territories from 1960-2008. We have added cascading expectation formation (in light of the Arab

Spring) and are adding international financial flows (in light of the 2008 financial crisis). We are calibrating the model to the Intergovernmental Panel on Climate Change (IPCC) 2000-2100 forecast referent to allow a common basis for comparing impacts.

Significance:
The DoD, DHS, and intelligence community are newly interested in having us help them understand the changes in risk and mission space from climate change. DOE has a renewed interest in our uncertainty quantifications and modeling methods. In accordance with Sandia's goals, this effort improves high-resolution climate modeling methods of critical importance to predictive science, develops advanced spatially and temporally resolved methods to enable discovery of phenomena, and develops new computational and statistical approaches for optimization, verification, validation, and uncertainty quantification necessary for regional predictions to enable national security assessments. The DOE Office of Science has, for the first time, now given Sandia funding for climate assessments and we have been invited as contributors and lead authors to the National Climate Assessment, facilitated by DOE and other organizations, and directed via the White House.

Streaming Data Analysis for Cyber Security
141511

Year 2 of 3
Principal Investigator: S. J. Plimpton

Project Purpose:
A ubiquitous task in cyber security is monitoring network traffic, looking for anomalies that indicate incoming attacks, intruders or malware already inside a local network, or data exfiltration. Monitoring typically involves data collection and post processing of archived logfiles using manually updated filters along with human inspection and judgment. While effective, this approach has limitations: timely responses may be impossible, analyses may be inaccurate or incomplete since data exceeds storage capabilities, and rapidly evolving strategies may be undetectable.

These issues can potentially be addressed by modeling and analyzing the stream of network traffic in real time, as it is captured. This is challenging due to the large volume of data, limited computational power in monitoring hardware, and a lack of mathematical definitions of interesting events and algorithms to detect them in streaming data. We are in the process of developing new streaming algorithms and software to overcome these challenges and enable the power of postprocessing methods, which employ graph-based algorithms and classification techniques, to be applied in real time. This project aligns with several of the national and Sandia goals; namely, quick detection and attribution of attacks, software development to ensure integrity of our cyber infrastructure, and threat analysis methods based on scalable informatics.

Summary of Accomplishments:
In the first two years of this project, we have worked to detect and capture interesting "events" in network packet flows. We have applied machine-learning techniques such as ensembles of decision trees to classify these events and identify high-impact features, concept drift over time, and occurrences of outliers. We are in the process of making our pipeline-processing framework accessible to cyber analysts at Sandia.

We have also formulated a novel parallel algorithm that can ingest a continuous stream of edges and store/expire a time-stamped graph across the aggregate memory of many processors. Real-time user queries can identify connected components within the graph and their attributes. We have partially implemented the algorithm in a new streaming framework called Parallel Harness for Informatics Stream Hashing (PHISH), which supports the exchange of small datums between independent, continuously running processes, either on the same machine or across a network. PHISH also allows a streaming MapReduce-style processing of large archived datasets.

Significance:
Sandia has made a strategic decision to emphasize cyber security. This project can contribute to two specific goals. The first is to become a "model laboratory" for DOE in information security, going beyond basic compliance. Having the tools at our disposal, which this project should create, is a step in that direction. Second, the report discusses a "super-defense" strategy for cyber security. The software produced by this project could be part of that solution.

The benefits of this work are practical, programmatic, and scientific. Our streaming algorithms on data collection hardware will enable Sandia (and others) to protect its network and sensitive data. Our collection of algorithms will be novel technology that Sandia can use to form partnerships in the intelligence community. More broadly, processing streaming data is a computational challenge gaining importance in many fields of security and science. For example, in financial transaction software, what we are attempting to do is termed "complex event detection." Cloud computing is also beginning to grapple with streaming algorithms, due to the immense volumes of data it can process. Success in this project would enable Sandia to become a leader in this emerging area.

As far as possible, given the sensitive use of this kind of software, we will publish our algorithmic work in the open literature. We also plan collaborations with academics working in the more general area of streaming algorithms.

Effective Programming Tools and Techniques for the New Graph Architecture HPC Machines
149655

Year 2 of 3
Principal Investigator: D. Dechev

Project Purpose:
Large graph problems that arise in complex network analysis, data mining, computational biology, and national security applications have sparked the development of new types of high performance architectures and codes. These codes involve very large numbers of threads and much greater sharing of information between processors than traditional scientific computing approaches, posing much greater concurrency challenges. Unfortunately, concurrent programming for shared memory multithreaded applications is nontrivial because of the numerous hazards including race conditions, deadlocks, livelocks, and order violations. Such errors are hard to reproduce, often lead to unpredictable real-time behavior, and are notoriously difficult to debug. The use of mutual exclusion, the most common synchronization technique for shared data, can lead to significant overhead, high complexity, and reduced parallelism in addition to the mentioned safety risks. Even for conventional multicore systems and datasets of modest size, the use of mutual exclusion can cause convoying effects that, in turn, can seriously affect the application's performance. According to a number of studies at National Aeronautics and Space Administration (NASA) Ames, the current development and validation techniques are prohibitively expensive for problems of such complexity. We are addressing this highly challenging problem by creating a software framework for safe and efficient concurrent synchronization for massively multithreaded shared-memory programs. This approach will be based on the application of lock-free synchronization, a new alternative to mutual exclusion for designing scalable data objects. In previous work, we have shown that lock-free synchronization eliminates whole classes of concurrency hazards while delivering performance improvements for many scenarios by a large factor. Our goal is to create a portable and generic software platform that will greatly assist domain scientists — who are not experts in concurrency theory and formal methods — to produce highly efficient and correct high performance computing (HPC) code for solving large graph analysis problems.

Summary of Accomplishments:
In the past year, we have completed and demonstrated the first design and implementation of a wait-free hash table. Our multiprocessor data structure design allows a large number of threads to concurrently insert, remove, and retrieve information. Nonblocking designs alleviate the problems traditionally associated with the use of mutual exclusion, such as bottlenecks and thread-safety. Lock-freedom provides the ability to share data without some of the drawbacks associated with locks; however, these designs remain susceptible to starvation. Furthermore, wait-freedom provides all of the benefits of lock-free synchronization with the added assurance that every thread makes progress in a finite number of steps. This implies deadlock-freedom, livelock-freedom, starvation-freedom, freedom from priority inversion, and thread-safety. The challenges of providing the desirable progress and correctness guarantees of wait-free objects make their design and implementation difficult. There are few wait-free data structures described in the literature. Using only standard atomic operations provided by the hardware, our design is portable; therefore, it is applicable to a variety of data-intensive applications including the domains of embedded systems and supercomputers. We have integrated and tested our wait-free data structure in a variety of mission spaces including the Matevo apps, the S3D combustion codes, and a variety of benchmarks. Our performance evaluation indicated that, when compared to the best available locking designs, our wait-free data structure demonstrates a performance speed-up by a factor of eight or more. When compared to alternative non-blocking designs, our hash table

demonstrates solid performance gains in a large majority of cases, typically by a factor of four or more. This wait-free hash table implementation will play an important role in our parallel implementation of a variety of graph algorithms, a multicore branch and bound search, and will have a significant impact on the design of exascale data structures and algorithms.

Significance:

This project ties to DOE's mission and strategy to advance the computational sciences and computational capabilities for today's frontiers of scientific discovery. Our approach will deliver high performance and increased safety for future HPC platforms and provide an alternative to current expensive and hazardous coding techniques for concurrent programming. Our research will eliminate bottlenecks and improve performance for advanced simulations, benefiting the DHS National Infrastructure Simulation and Analysis Center, as well as the intelligence and scientific computing communities.

Stochastic Study of Microparticle Adhesion due to Capillary Condensation
150123

Year 2 of 3
Principal Investigator: J. A. Hubbard

Project Purpose:
The purpose of this project is to combine Sandia's expertise in experimental and computational sciences to advance the state of knowledge on microparticle adhesion and interfacial physics. Ultimately, knowledge gained here will provide a foundation on which to predict rates of aerosol resuspension, develop aerosol transport models, and facilitate technological development in the area of trace detection of CBRNE (chemical, biological, radiological, nuclear, and explosive materials). This project is collaborative by nature, seeking to forge new relationships which enable fundamental science and discovery through interdisciplinary research. Advanced diagnostic tools from the Aerosol Measurement Laboratory and Microdynamics Laboratory have been combined to study microparticle adhesion with new and innovative methods. Large experimental uncertainties exist in data from previously published works. These uncertainties have limited progress in the field due to inabilities to accurately characterize systems of practical interest. The effects of capillary forces and van der Waals forces will be quantified to address deficiencies in data concerning adhesion in realistic ambient environments (e.g., high relative humidity). Experimental methods and diagnostics used here will reduce experimental uncertainty, thereby providing highly resolved validation data for Sandia's computational tools. Experimental techniques and models developed in this study will then be applied to national security problems like bioaerosol resuspension and trace detection of CBRNE to serve in the national interest.

Summary of Accomplishments:
We have combined diagnostic tools from Sandia's Aerosol Measurement Laboratory and Microdynamics Laboratory to study microparticle adhesion with innovative experimental methods. The combination of diagnostic tools has led to observations of novel particle-surface phenomena. Procedures were developed to deposit a uniform layer of monodisperse particles on semiconductor grade wafers. Wafer substrates were then excited ultrasonically and particle dynamics were observed with microscopy and high-speed imaging. The distinguishing characteristic of this study is the use of laser Doppler vibrometry (LDV) to accurately characterize surface kinetics which causes particle motion. At high surface accelerations, particles are observed to bounce on the surface. This phenomenon was used to quantify the effects of capillary condensation on the stochastic nature of particle removal in realistic ambient environments. At lower accelerations, particles exhibited a quasi-two-dimensional diffusive motion analogous to diffusion-limited-cluster-aggregation seen in colloids and aerosols. Aggregation kinetics have been quantified and show characteristic diffusion times are a function of surface acceleration, excitation rate, and aggregate size. Aggregates also possess fractal character which has been quantified through reciprocal space methods. Lower surface accelerations result in more tenuous aggregate structures as particle kinetics approach the quasi-two-dimensional limit. Structural dynamics of aggregates have also been characterized with LDV and show the unique and significant effect of cohesive forces on aggregate adhesion. Aggregates which appeared stationary in the two-dimensional plane (parallel to the surface) were actually comprised of individual particles exhibiting out-of-plane oscillations on the order of 50 nanometers. This changes our fundamental perspective of aggregate behavior on a surface. Cohesive interactions affect adhesion through the dissipation of removal forces and subsequent restructuring of aggregate particles.

This study has produced many fundamental results of interest to the S&T community. This is the first work to experimentally observe quasi-two-dimensional-diffusive-cluster aggregation on a planar surface. We have observed the effects of interparticle cohesive bonds on the adhesion of aggregates with complex morphological properties. Previously, one might have assumed a 10-micrometer aggregate responded to aerodynamic forces similarly to an individual 10-micrometer particle. This is not the case, and was characterized for the first time here with the use of LDV. Adhesive and cohesive forces are, therefore, hypothesized to strongly affect adhesion an aggregate may dissipate applied forces and subsequently remain adhered when single particle theories suggest otherwise. This is particularly relevant to the detection of biological weapons agents since few particles are likely to exist as isolated monomers.

Significance:
Sandia's investigation of the 2001 anthrax attacks on Capitol Hill revealed aggregates on the order of 10 micrometers consisting of thousands of individual anthrax spores. Biological identification technologies rely on the mass of biological material collected. Liberating an aggregate of this size from the surface thereby yields one thousand times more diagnostic material than an individual spore. Understanding how these agglomerates adhere is critical to formulating detection and remediation protocols and designing efficient removal technologies. Sandia's computational physics tools are uniquely capable of modeling these phenomena. In this study, we also examined the influence of relative humidity on the stochastic nature of particle removal. This is relevant to the detection of chemical, biological, radiological, nuclear, and explosive material (CBRNE) in realistic ambient environments. This work suggests particle removal is infeasible for capillary forces five times higher than the removal force. These types of empirical correlations are broadly applicable in the development of risk assessment tools and reaerosolization models.

Studies in High Rate Solidification
150638

Year 2 of 3
Principal Investigator: J. D. Madison

Project Purpose:
Sandia is responsible for the quality and well-being of welding and brazes in various engineering components. High rate solidification joinings are multitiered, multiphysics processes. Prior investigations have focused primarily on macroscale studies beyond the level of the microstructure and have been largely phenomenological and process-driven in scope. While still challenging, three-dimensional reconstructions of experimentally derived microstructures of appreciable scale and resolution are becoming increasingly possible due to recent advances in experimental tools, computational power, and data storage.

The purpose of this project is to investigate the linkage between processing and resultant microstructure among high rate solidification events found in welds. Simulation tools developed at Sandia, previously used to examine the effect of macrostructure and its effect on mechanical properties are being extended to evaluate a smaller length scale. The presence, variability and distribution of microstructural features such as porosity are being examined for determination of impact and effect on joint stability, integrity, and composition while being related to process parameters such as weld speed and mode. Microstructural three-dimensional reconstructions and characterization are being pursued to provide representative metrics for simulation domains.

Summary of Accomplishments:
We developed qualitative and quantitative characterization tools for qualifying welds in 304L Stainless Steel. Investigation has focused on millimeter-scale welds applicable to typical NNSA & DOE use, such as component enclosures and pressure vessels. In FY 2011, the following capabilities and results were accomplished: We developed and demonstrated a method to nondestructively measure the following in millimeter-scale welds:

- Porosity per unit length
- Nominal void volume
- Specific void volume distributions
- Total void volume fraction
- Quantitative representation of collective void morphology per weld

The expertise and tools developed in this project were also leveraged to address porosity characterization needs and grow collaborations with other Sandia investigations.

Significance:
Sandia is responsible for the quality of welds and brazes throughout the DOE/NNSA with applications ranging from nuclear weapons and energy to waste storage and renewable energy. This work has direct applicability to life extension efforts in deep welds of precipitation hardened martensitic steels and the employing of nitrogen strengthened stainless steels. However this work will also allow improvement in Sandia's ability to support welds and joinings throughout the entire DOE/NNSA complex. A practical and immediate use of the findings are in the process parameter maps which have been generated to date that indicate porosity amounts, size, shapes as a function of weld power and speed. These same maps also indicate weld shape, surface dimensions, and internal subsurface dimensions also based upon weld power and speed in edge joints in 304-L stainless steel.

Quantifiably Secure Power Grid Operation, Management, and Evolution
151288

Year 1 of 3
Principal Investigator: J. Watson

Project Purpose:
This project will develop decision-support technologies to enable rational and quantifiable risk management for key grid operational and planning timescales.

Risk or resiliency metrics are foundational in this effort. The 2003 Northeast Blackout investigative report stressed the criticality of enforceable metrics for system resiliency — the grid's ability to satisfy demands subject to perturbation. However, we neither have well-defined risk metrics for addressing the pervasive uncertainties in a renewable energy era, nor decision-support tools for their enforcement, which severely impacts efforts to rationally improve grid security. For second-to-minute timescales, robust control systems must mitigate the impact of failure cascades, forming self-sustaining island network topologies to facilitate rapid service restoration. For day-ahead unit commitment, decision-support tools must account for topological security ("N-K") constraints, loss-of-load (economic) costs, and supply and demand variability — especially given high renewables penetration. For long-term planning, transmission, and generation, expansion must ensure that realized demand is satisfied for various projected technological, climate, and growth scenarios.

Our decision-support tools will analyze and enforce tail-oriented risk metrics for explicitly addressing high-consequence events, drawing from recent work in computational finance. Historically, decision-support tools for the grid consider expected cost minimization, largely ignoring risk and, instead, penalizing loss-of-load through artificial parameters. Our technical focus is the development of scalable solvers for enforcing risk metrics. We will develop advanced stochastic programming solvers to address generation and transmission expansion and unit commitment, minimizing cost subject to pre-specified risk thresholds. Despite significant promise, major algorithmic challenges remain to address regional and national grid scales. With renewables, security critically depends on production and demand prediction accuracy. We will use powerful filtering techniques for spatiotemporal measurement assimilation to develop short-term predictive stochastic models. Novel robust control algorithms will be developed to enforce risk thresholds for unit commitment and failure cascade mitigation. These algorithms currently and unrealistically (given renewables) assume tightly bounded uncertainties.

Summary of Accomplishments:
We have implemented stochastic unit commitment solvers using our Coopr open-source software library. Unit commitment is the core optimization model associated with day-to-day grid operations. We are beginning to experiment with large-scale, real-world data — critical for assessing solver scalability. Toward this effort, we have extended a Sandia Cooperative Research and Development Agreement (CRADA) with a Western US electric utility to study high-penetration renewables scenarios using our solver technology and their data. Our solver technologies have also formed the basis for a recently submitted ARPA-E (Advanced Research Projects Agency-Energy) proposal for advanced unit commitment strategies. Over the past six months, we have significantly strengthened 6100-1400 interactions on grid R&D, leading to both algorithmic, data, and proposal collaborations.

We continue to work with Iowa State University on stochastic generation expansion models. We recently published a journal paper describing our research to date (Energy Systems, Springer).

We have developed algorithms for dramatically reducing the solution times for network design problems requiring "N-K" security (i.e., networks that must be resilient to the loss of K from a total of N components). We are working toward integrating this algorithm into core grid optimization models and solvers, including unit commitment, transmission expansion, and generation expansion. We have participated (via invited talks, one of which will be plenary) in a variety of external conferences relating to the grid operations and planning, and specifically the role of optimization in these models. Long-term interactions with the University of Florida and Arizona State University have been initiated, to support our stochastic unit commitment research.

Significance:
Recent DOE strategic plans call out national energy security as a primary responsibility, indicating the need to "Facili[tate] the process to modernize the electric grid" and "enhanc[e] security and reliability of the energy infrastructure." Additionally, these plans point out the need to improve "domestic energy security . . . through . . . increasing reliability and productivity." The risk-informed decision tools directly address these needs, in particular, emphasizing the objective of rational modernization of the grid while simultaneously improving reliability and resiliency. Further, these tools will facilitate policy assessment and development in support of national energy objectives. Scalable stochastic unit commitment solvers are of significant interest to utilities through the US and world. Presently, these solvers are not scalable, impeding the cost-effective adoption of renewables — especially in high-penetration scenarios.

Refereed Communications:
J.-P. Watson, D.L. Woodruff, and W.E. Hart, "PySP: Modeling and Solving Stochastic Programs in Python" to be published in *Mathematical Programming Computation*.

S. Jin, S.M. Ryan, J.-P. Watson, and D.L. Woodruff, "Modeling and Solving a Large-Scale Generation Expansion Planning Problem under Uncertainty," to be published in *Energy Systems*.

Predicting Structure-Property Relationships for Interfacial Thermal Transport
151289

Year 1 of 3
Principal Investigator: E. S. Piekos

Project Purpose:
Microsystems are a key component in a vast array of applications, impacting most Sandia mission thrusts. Over time, microsystems designers have increased the number of material regions in a typical device while decreasing their spatial extent. From a thermal perspective, this trend increases the relative importance of interfacial transport compared to traditional bulk transport. Increasingly, interfacial thermal transport is an important factor in numerous Sandia-developed microsystems including high-power electronics, coolers for space-based sensors, microelectromechanical system (MEMS), and thermoelectric power modules. Predictive tools are, therefore, essential for characterizing existing designs under uncertainty in manufacture and operation, as well as for leveraging interfacial transport to enhance functionality in future designs.

Current models for interfacial thermal transport are inherently limited due to the nearly ubiquitous assumption of a perfect boundary. As a result, the transport is treated as an intrinsic material property, independent of interface structure, despite ample experimental evidence to the contrary. We are working to develop a predictive tool for thermal transport through realistic interfaces. This tool will provide experimentally validated structure-property relationships for nanostructural features, including interfacial dislocations and compositional intermixing. It will be developed through a “bottom-up” computational approach, combined with systematic fabrication, disruption, and characterization of interfaces.

Interfacial thermal transport at imperfect boundaries is an inherently multiscale problem with many interacting effects arising from the fact that lattice perturbations can extend over many unit cells and many types of defects can exist simultaneously. An organized inquiry, therefore, places great demands on simulation, sample fabrication, microstructural characterization, and thermal transport measurement — all of which must be performed in close communication with one another to disentangle competing effects. Sandia’s strength in all these areas provides a unique opportunity to perform such an inquiry and replace decades-old simplifications with validated physics-based models.

Summary of Accomplishments:
A new model for predicting frequency-dependent phonon transmissivity at interfaces between dissimilar materials — called the lattice mismatch model (LMM) — was developed. This compact model produced excellent agreement with far more expensive molecular dynamics simulations.

Two sets of parametrically varied interfaces were fabricated on silicon wafers. In the first series, 80/20 SiGe films of thickness from 10 to 310 nm were grown. In the second series, 150-nm SiGe films, with composition varying from pure Si to pure Ge were grown. In both cases, stresses produced by lattice mismatch will create dislocations at the film/wafer interface. Ultrafast Raman spectroscopy measurements have begun on these samples, as well as structural imaging with transmission electron microscopy (TEM). The TEM images have shown the expected stacking faults at the interface and an unexpected twist: the faults extend into the substrate. Additional characterization of the range of produced samples will allow a detailed understanding of the interfacial structure of these materials, and its effect on thermal transport, to be developed.

Silicon and sapphire substrates were subjected to proton irradiation at various doses prior to deposition of an aluminum layer to study the effect of structural disorder on interfacial transport. Thermal transport across these interfaces was measured with time domain thermoreflectance and a two-parameter model was developed to relate the observed interface conductance to the proton dose. Comparing the parameters in the model between the two material combinations measured, one parameter was related to the bulk modulus and the other to the calculated displacements per atom per unit volume. With data from additional materials, this result could provide a path to a predictive model.

Significance:
Interfacial thermal transport is a significant performance determinant for a variety of microsystems throughout the DOE and broader national security mission space, including efforts in microelectronics, microelectromechanical systems, solid-state lighting, thermoelectrics, and sensors. Despite this fact, previous simulations have been unable to link the structure of a particular material junction to its thermal performance. Through this project, we will remove this limitation, thereby enabling predictive simulation of microsystem performance and increasing functionality by placing enhanced understanding of thermal transport through nanoscale features in the hands of designers.

Refereed Communications:
P.E. Hopkins, T.E. Beechem, J.C. Duda, K.M. Hattar, J.F. Ihlefeld, M.A. Rodríguez, and E.S. Piekos, "Influence of Anisotropy on Thermal Boundary Conductance at Solid Interfaces," *Physical Review B*, vol. 84, p. 125408, September 2011.

P.E. Hopkins, K.M. Hattar, T.E. Beechem, J.F. Ihlefeld, D.L. Medlin, and E.S. Piekos, "Reduction in Thermal Boundary Conductance due to Proton Implantation in Silicon and Sapphire," *Applied Physics Letters*, vol. 98, p. 231901, June 2011.

Physics-Based Multiscale Stochastic Methods for Computational Mechanics
151291

Year 1 of 3
Principal Investigator: J. B. Lechman

Project Purpose:
Classical continuum models of transport in complex, heterogeneous systems (groundwater contaminant transport, charge carrier transport/storage in composite electrodes) frequently struggle to give reliable results while detailed microscopic methods (molecular dynamics) are computationally prohibitive at large scales. However, it is often unrecognized that these systems exhibit related phenomenology that can serve as a unifying basis for generalization of continuum mechanics beyond classical assumptions. Common features include long-range correlations and multiple overlapping/competing length and time scales, rendering the classical assumptions of scale separation and "slowly" varying mass, momentum, and energy densities suspect. Yet, recent developments in nonlocal models make relaxation of classical assumptions possible without sacrificing mathematical verification, computational feasibility, or model validation. Hence, we seek nonlocal models that are thermodynamically and physically consistent at scales intermediate to the atomistic and component/process (macro) scales. As an archetype, we are developing a physically based, mesoscale, stochastic continuum model of colloidal suspensions in heterogeneous environments (diffusive transport in random media).

Although much recent effort has focused on elucidating spatial and temporal nonlocality and its effects in various systems, we seek to develop models in the framework of nonlocal calculus and nonlocal diffusion equations. This is a novel approach that distinguishes Sandia's capabilities. In particular, it avoids assumptions that create difficulties for capturing inherently nonlocal phenomena (e.g., "cooperative"/correlated dynamics, or non-Fickian behavior). Many efforts seek to capture these effects through higher-order gradients in expansions of relevant fields, or through homogenization. We seek to capture nonlocal effects through integral equation formulations as opposed partial differential equation–based models. A high-risk focus of this effort will be establishing the physical basis of the approach in terms of correlation lengths and times and the link between microscopic correlated dynamics and mesoscale statistics for the model system.

Summary of Accomplishments:
To begin the project, we selected a simple model heterogeneous system that would exhibit multiple time and length scales. We selected hard-sphere colloids suspended in a Newtonian fluid. This allows for varying the volume fraction of colloids as the "control knob" for varying the amount on non-Fickian, or anomalous (sub) diffusion. We quickly determined that systems such as this, which exhibit subdiffusive behavior, can be described by a nonlocal time formulation of a Langevin equation. Hence, we proceeded to formulate a Generalized Langevin Equation (GLE) model of the same system based on transient Stokes fluid flow and fractional Brownian increments. We are implementing this model in the large-scale atomic/molecular massively parallel simulator (LAMMPS) code.

In the meantime, we performed a series of simulations without transient flow (i.e., making the Markov assumption and simulating with the classical Langevin equation), but being careful to include the pair-force interactions between colloids. The pair-force represents a nonlocal interaction and the functional form of this interaction represents a position-dependent constitutive relation. By analyzing the simulations, we have learned that we can convert the position-dependent nonlocal colloidal interactions into time-dependent nonlocal interactions. Thus, the colloidal pair-potential can be reformulated into a memory kernel for use in a GLE and that can be determined directly from experiments. Finally, we have learned how to relate this "microscopic" memory kernel to the macroscopic rheological response.

On the experimental side, we aim to validate all the previous findings and advance the state-of-the-art of analysis techniques for diffusive wave spectroscopy (DWS). To this end, we have built a DWS machine and are ready to begin collecting data on a model hard-sphere system.

Significance:
This work has relevance to the DOE energy security mission through providing mesoscale models and capabilities applicable to composite electrode energy storage devices and to nuclear waste forms and groundwater contaminant fate and transport (also, environmental responsibility). Sandia's national security mission is impacted through application of these methods to energetic materials for DoD and NNSA interests. Specifically, understanding how to model the microstructural response of heterogeneous materials to insults and loadings is critical to predicting and controlling performance of energy storage devices and energetic materials. We have begun to pursue collaborations with makers of energy storage devices to give them insight into the connection between rheology and microstructure of their formulations, which is their primary metric for quality control of electrodes. However, this metric can yield widely varying results in performance. Additionally, the techniques developed here will advance the science and technology base of nanoengineering and manufacturing by providing tools for rational design and manufacturing of tailored nanocomposites. Such innovative materials have great promise to revolutionize device functionality and, thereby, the US manufacturing base and economic security.

Refereed Communications:
N. Burch and R. Lehoucq, "Continuous-Time Random Walks on Bounded Domains," *Physical Review E*, vol. 83, p. 012105, January 2011.

R.B. Lehoucq and M.P. Sears, "Statistical Mechanical Foundation of the Peridynamic Nonlocal Continuum Theory: Energy and Momentum Conservation Laws," *Physical Review E*, vol. 84, p. 031112, September 2011.

Network and Ensemble Enabled Entity Extraction in Informal Text (NEEEEIT) 151292

Year 1 of 3
Principal Investigator: W. P. Kegelmeyer

Project Purpose:
Much of the world's actionable information is locked up in increasingly unmanageable volumes of text. This has inspired work in "entity extraction," which is the detection of meaningful terms in text: persons, places, dates, etc. Robust, accurate entity extraction is the crucial first step for all information extraction from text: one cannot "connect the dots" unless the dots are identified in the first place.

Entity extraction has thus far focused on clean, edited, "forma" text. Unfortunately, much of the information of interest is in personal, "informal" text, such as email or blogs. These differ from the Medline abstracts and Reuters news stories commonly studied in that they tend to be riddled with errors of spelling and grammar, abbreviations, and a terseness and obliqueness of reference resulting from the context shared by sender and receiver. The informal text domain has received scant study; just enough to show that it causes the performance of existing methods to drop precipitously.

We intend to vastly improve the accuracy of entity extraction in informal text, via application of Sandia-specific expertise in "ensemble" machine learning methods. Further, we will exploit new high performance computing network capabilities to permit the "integrated" analysis of a full conversational thread. The potential of this approach is recognized, but scaling issues have, prior to recent Sandia work, prevented their exploration. By creating methods to make accurate entity extraction in informal text possible, and by leveraging Sandia's investment in the Titan informatics framework, we will deliver a system that starts with raw email or blogs and produces high-quality entity identification, suitable for search, linking, visualization, and analysis.

Summary of Accomplishments:
We completed a literature review to establish our base entity extraction methods and features, and to organize our initial software investments. It also led to the insights that: 1) there is a need for a "terminology and methodology" paper to provide a unified description of the variety of poorly differentiated existing conditional random field (CRF) idioms and evaluation methods, and 2) that grounding ensemble methods as sampling from the structure of a graphical model promises to both unify existing ensemble methods and to guide research into new ones.

We have acquired and converted an email corpus. We have extracted baseline features (for comparison to prior published work), rich features (to use all available information), and new features based on the email metadata. We have coded an extensive algorithm experiment and evaluation infrastructure. The code base is flexible and heavily instrumented, supporting capture and retrospective analysis of almost all aspects of the analysis experiments. The most computationally demanding parts include parallel implementations leveraging distributed memory, threading, and client-server approaches.

In terms of assessment and impact, we have consulted with Sandia's national security analysts, and have acquired an open dataset that serves as an unclassified surrogate for one of their concerns. The main insight here is that entity extraction used to improve "sentiment" assessment would be both a new research direction and have practical use. We have further begun to assess our progress by measuring the utility of entity extraction as a pre-processing step for categorization of text.

Finally, we have implemented and evaluated all the best-practice ensemble methods for non-CRF classifiers, and have developed CRF-suited variations, as well as a new method, "coarse CRFs." One resulting insight is that a CRF operates on a sequence, while accuracy is based on tokens, requiring unexpected and promising generalizations of existing ensemble concepts.

Significance:

Much of the world's most specific, useful, and actionable information is in informal, shared-context communications, such as email and blogs. This information is critical to analysts who seek to connect specific dots or to develop a broad situational awareness, but is rendered unreachable both by its sheer volume and by the extra, and so far unaddressed, text analysis challenges posed by its very nature. We are working to meet those challenges, to develop novel and scalable methods, implemented in practical software, to reach that unreachable information, and so provide Sandia with a unique capability to support our intelligence-analyst community.

Kalman-Filtered Compressive Sensing for High-Resolution Estimation of Anthropogenic Greenhouse Gas Emissions from Sparse Measurements at Global Scale
151293

Year 1 of 3
Principal Investigator: J. Ray

Project Purpose:
Characterization of the global spatiotemporal distribution and dynamics of anthropogenic and biospheric CO_2 fluxes is a critical aspect of carbon cycle science and will form an important component in the verification of anticipated international treaties and management of mitigation programs. Similar to other problems at Sandia and throughout the scientific community, accurate source characterization depends on the numerical prediction of complex dynamics, conditioned on limited observations, with simultaneous quantification of uncertainties. A so-called "inversion" problem can be formed that reconstructs the location/character of CO_2 emissions and sequestration by minimizing the difference between observations and predicted values, subject to other known constraints. Many technical challenges arise, however: 1) large, ill-conditioned linear systems result from sparse measurements and complex diffusive dynamics, 2) extreme computational resources are required to address the high dimensionality of the uncertainty space, 3) a consistent and complete statistical framework is necessary for characterization of uncertainty, and 4) an ability to accommodate massive measurements obtained at various scales is required. This project addresses these issues through adaptation of novel image reconstruction techniques, efficient data assimilation methods, multiscale algorithms, and geostatistical Bayesian inverse methods.

We are working to develop Bayesian techniques to reconstruct time-variant, spatial fields from limited measurements, by integrating concepts from compressive sensing (CS), Ensemble Kalman Filters (EnKF) and multiscale modeling. CS exploits sparse basis sets to achieve accurate multiscale field/image reconstruction from limited data. We will extend these approaches to dynamic fields such as CO_2 fluxes, and integrate these techniques with efficient data assimilation methods. To this end, EnKF provides the necessary balance of computational efficiency and robust uncertainty characterization, as well as an avenue to explore assimilation of multiscale observations. Our algorithmic development will focus on supporting the CO_2 source flux estimation problem as a fundamental technical capability but will be sufficiently general to be directly relevant to many problems in science and engineering.

Summary of Accomplishments:
We have focused on identifying an efficient basis set for representing anthropogenic emissions for use in inversions. To do so efficiently, we have developed a convection-diffusion (CD) simulation prototype coupled to an EnKF. The prototype has been used to perform inversions as well as to generate synthetic data, using CO_2 emissions patterned on nightlight images from Defense Meteorological Satellite Program-Operational Linescan System (DMSP-OLS). To enable inversions at high spatial resolutions, we have explored both multiresolution bases and kernel-based representations of spatially resolved CO_2 emission fields. We found that Haar wavelets provided the sparsest representation of 2002 US anthropogenic emission fields, available from economic and socioeconomic information (Vulcan database).

Since our objective is to enable realistic CO_2 inversions with our algorithmic developments, we have also obtained and customized a parameterized chemistry transport model (PCTM), from National Aeronautics and Space Administration (NASA)/Goddard, for CO_2 dynamics. PCTM, coupled to EnKF, will serve as the forward model in our inverse problem. The model is driven by reanalyzed wind fields (700 MB of data per day). Currently, we are validating the customization (automating the processing of MERRA [Modern Era Retrospective-analysis for Research and Applications] files, identification of resolution, etc.) with a view of performing transport simulations using data from 2008-2011. In order to enable inversions from sparse observations, we have investigated three competing reduced-order representations of US CO_2 emissions. The first model involves using multiresolution bases, under two sparsity-enforcing priors: 1) nightlights acting as a spatial prior and 2) Laplace distributions. This has been compared against representations obtained with Gaussian kernels and blended interpolations between pilot points, both fitted to nightlight images. These reduced-order representations of US CO_2 emissions are used within the context of an inverse problem with synthetic data.

Significance:
This project will demonstrate the use of a novel multiscale random field model in the reconstruction of nonstationary fields. Such problems occur within the context of remote sensing in nonproliferation treaty verification, material property identification, and management of CO_2 sequestration reservoirs. It can also be used to reconstruct the adjacency matrix of a network, modeled as a field, and be applicable to computer network/botnet tomography. In addition, this project will position Sandia as a key contributor to attribution efforts for Greenhouse Gas Information Systems, which are expected to play a central role in an abatement treaty verification process.

Tangibly, the project will result in the creation of software implementations of the random field model, and the means of enforcing sparsity, when fitting it to data. These models and sparsity priors are general and can be used in a number of settings/applications, as specified above. In addition, the algorithms used to fit the multiscale random field model to data (namely ensemble Kalman filters, EnKF), will be implemented to function in a massively parallel setting, to offset the computational cost of running an ensemble of atmospheric transport models. EnKFs are used in many data assimilation problems and a parallel, general-purpose EnKF implementation will find use in a number of Sandia projects, particularly in the field of parameter estimation or uncertainty quantification.

Multiscale Modeling for Fluid Transport in Nanosystems
151294

Year 1 of 3
Principal Investigator: J. A. Templeton

Project Purpose:
Nanoscale fluid transport processes play an important role in the performance of many nanosystems, such as batteries, supercapacitors, and chemical detectors. The commonalities in these devices involve nanoscale interactions between a fluid/solid interface and an attached larger bulk reservoir. Interaction with the bulk critically affects the performance of the nanosystem because the fluid can exhibit drastically different behavior at different scales. Two-way feedback between the scales is required to predict system behavior. For example, high-voltage double layers in energy storage devices deplete bulk electrolyte concentrations, thereby modifying ion transport to the double layer. Molecular dynamics can resolve the complexity of nanodevices, but is intractable for the bulk, which requires continuum methods. New algorithms capable of capturing the relevant physics for accurate device simulation are needed to account for time-dependent mass, momentum, and thermal transport between these scales.

We are developing a novel multiscale coupling technique between atomistic representations of the fluid/nanostructures with connected reservoirs modeled using finite elements. Our work will focus on many features encountered in real problems: a reservoir interacting with nanostructured interfaces, electrically conducting and insulating surfaces, multiple species, and chemical reactions. We are first designing interscale operators appropriate for fluid transport that bridge atomistic and continuum scales to form the foundation of coupling algorithms based on mass, momentum, and energy conservation. Our algorithms will enable both time-dependent and time-averaged coupling between the bulk and nanoscales — a significant advantage over existing methods. Multiscale electric field effects will be included for simulations of powered nanodevices, while chemical reactions will augment the multiphysics capabilities. A key differentiating aspect of our approach is the exertion of an atomistic coupling force based on conserved quantities (e.g., momentum, energy) only near the atomistic/continuum interface. This technique will be appropriate for complex molecules, whereas existing methods are limited to atomic fluids due to difficulties prescribing all degrees of freedom for multiatomic particles.

Summary of Accomplishments:
We have developed and performed preliminary testing on two of the key capability deliverables in this work. Our objective was to develop coarse-graining operators spanning the Lagrangian frame of the atoms and Eulerian frame of the continuum. We adapted our existing interscale operators for this purpose. Doing so required developing an entirely new time integration strategy. Ideas from traditional continuum fluid solvers were applied to this problem in new ways; specifically, different update methods for different terms in the governing partial differential equations and a fractional step method to exactly enforce the constraints coupling the molecular dynamics (MD) and finite element (FE) models. Within this framework, we have developed the capability to apply fixed temperature and energy flux constraints. We have also begun work developing and implementing a new method to provide electrical boundary conditions to MD typical of conditions present in electrical energy storage devices. We have adjusted our schedule to take advantage of synergistic experiments which can be used to validate our techniques. These experiments measure the electrical field within an electric double layer at distances nearer the surface than currently possible. Our original validation plans involved using coarser measurements to infer the correctness of our simulations, but now we will be able to directly compare quantities between simulation and experiment. We have, therefore, been working on methods that can

dynamically determine the correct charge on a surface based on its electrical properties and the distribution of fluidic charges. Our plan is to relate these charge distributions to the experimental environment to enable direct comparisons against our models. A preliminary version of these techniques has been implemented and used to distribute charge to surface atoms based on a perfectly conducting substrate.

Significance:

This project is generating a new set of widely available capabilities enabling analysis and design of systems relevant to DOE and national security missions. Motivating our work are electrical energy storage devices for nuclear weapons, fuel cells, and biofuel synthesis for CO_2 mitigation and energy independence. We are collaborating with an experimental project that will help validate our methods and provide examples of how these methods can be used to generate knowledge of real systems. Additional applications include compact sensors for chemical/biological threat detection, ion removal for water purification, autonomous drug delivery and health monitoring in DoD applications, and thermal management solutions for nanoelectronics. The methods developed in this project will be general, so they can be used in other applications as appropriate. To facilitate this process, we develop the methods as a package in the Sandia's large-scale atomic/molecular massively parallel simulator (LAMMPS) code to distribute the results of this work to the open source community.

Statistically Significant Relational Data Mining
151295

Year 1 of 3
Principal Investigator: C. A. Phillips

Project Purpose:
In many data mining applications, especially the search for “unexpected” or “significant” structure in graph-based social information, it is difficult to specify exactly what one is looking for. For example, given a graph where nodes represent people and edges represent relationships between people, there is general agreement that a community is a set of nodes more connected internally than to the rest of the graph. But no formal graph theoretic definition of connectedness seems to capture what a human perceives to be the correct communities in all cases. Most community-detection algorithms combine approximate optimization of a metric with ad hoc statistical methods. To date, there are no rigorous ways to determine whether an algorithm has succeeded in finding the “correct” answer in a real data set, or even in specially constructed benchmarks. Similar questions arise in other graph-data-mining problems that search for specific patterns or attempt to explain (dynamic) relationships.

We are developing statistically rigorous methods for understanding and testing the significance of graph properties and structures. These methods can be incorporated into data mining algorithms either integrally, or as a postprocessing “acceptance” test. We will develop methods to create benchmarks for specific data mining problems that hide a known solution without destroying it. These benchmarks would provide confidence in algorithms’ absolute and relative performance.

Bayesian methods offer one plausible approach. Each graph problem provides unique challenges. We must formally describe a priori domain knowledge and constraints (“prior distributions”). We must create plausible random graph models, describing ways a community, pattern, etc. might evolve from these distributions. Then we must compute conditional probabilities that characterize the most likely solutions given the structure of the input instance. Although the general methods are well known to statisticians, they require customization to the structure of each problem. These methods have not been applied to evaluating the correctness of efficient graph algorithms.

Summary of Accomplishments:
We developed a new distributional model for graphs, where the community structure is an underlying model parameter that impacts the random presence/absence of graph edges (the data). This model permits other parameters, such as a random “mixture,” whereby some nodes behave purely randomly and do not belong to any community. This modeling framework allows observed edge relationships to inform statistical inference on the unknown communities. For this, we developed a new Bayesian analysis that places prior distributions on graph communities (complex node partitions) based on the Chinese Restaurant Process. The Bayes approach involves a novel, provably correct Markov Chain Monte Carlo (MCMC) sampler to allow calculation of posterior distributions for arbitrary quantities of interest (e.g., probability that two nodes are in the same community). We verified these methods and created model diagnostics on the classic college football data set: inferring conference membership from game schedules.

We designed another statistical model for networks where communities might overlap. We have a method to fit the parameters to a specific (real data) graph and then generate other graphs similar to it in linear time. This set of graphs can serve as a community-detection benchmark, provided we can measure performance across a suite of such graphs.

We identified three active applications for approximate pattern matching in graphs: discovering structural function in organisms (for biowarfare response), extracting high-level features (such as multibuilding facilities) from satellite images, and chemical design. Investigating multiple rigorous application-specific definitions of approximate matching is the first step to a general theory. We have acquired a community-detection challenge dataset with no ground truth.

Significance:
The benefits to the general S&T community are more rigorous algorithms and more rigorous evaluation of algorithms in the exploding volume of research on graph-based data mining.

Our methods could provide higher confidence in the correctness and performance of graph algorithms supporting applications of national interest. A graph derived from computer network traffic can represent relationships between external entities. Mining that graph can suggest candidate adversaries and anomalies worthy of investigation as cyber attacks. Network alignment can track the evolution of such graphs through time, providing some confidence as to whether changes are relevant and significant/real. Finding approximate matches in a graph has applications in nonproliferation, satellite imaging and reconstruction of (biological) metabolic pathways. There may be future applications in alternative biofuels. Connection subgraphs arise in counterterrorism applications.

We have identified a classified graph analysis application that could also benefit from the methods we are developing. The methods explored in the project have already impacted the technical solutions in a sensitive national security application.

Refereed Communications:
M. Rocklin and A. Pinar, "Computing an Aggregate Edge-Weight Function for Clustering Graphs with Multiple Edge Types," in *Proceedings of the 7th Workshop on Algorithms and Models for the Web Graph (WAW10)*, December 2010.

M. Rocklin and A. Pinar, "Latent Clustering on Graphs with Multiple Edge Types," in *Proceedings of the 8th Workshop on Algorithms and Models for the Web Graph (WAW11), May 2011*.

J.W. Berry, B.A. Hendrickson, R.A. LaViolette, and C.A. Phillips, "Tolerating the Community Detection Resolution Limit with Edge Weighting," *Physical Review E*, vol. 83, p. 056119, May 2011.

Integrated Nano and Quantum Electronic Device Simulation Toolkit
151297

Year 1 of 3
Principal Investigator: R. P. Muller

Project Purpose:
The next generation of semiconductor devices must confront quantum mechanical effects. These include both phenomena to be avoided, like gate leakage, as well as new behavior that can be harnessed, like entanglement. Few electron nanodevices have been developed to use entanglement in quantum computing and sensing beyond the traditional quantum limits, but the resulting entangled device states are extremely sensitive to atomic-scale effects such as surface roughness, which are not traditionally considered in nanoelectronics modeling. The community is presently without a multiscale simulation capability that appropriately captures how atomic-scale phenomena propagate through to the mesoscale device physics.

To properly describe these devices, we need to enhance existing device simulators in several ways. At the very least, the quantum mechanical wave function of single particles must be accounted for by solving the coupled system of the Schrodinger and Poisson equations. Where atomic-scale effects, such as the multiple valleys in silicon, are important, tight binding solutions for electronic wave functions are necessary for predictive simulations. Furthermore, in systems with many electron-excited states, configuration interaction techniques are needed to properly capture multi-electron wave functions.

We are developing a suite of tools that includes Schrodinger-Poisson, tight binding, and configuration interaction capabilities and thereby addresses current and future issues critical to simulating quantum-scale electronic devices. Although commercial semiconductor technology computer aided design (TCAD) tools are widespread, these tools are expensive, not parallel, limited by the number of finite elements in the simulation, and contain primitive, if any, quantum device modeling capabilities. Even the best and most expensive tools lack the ability to simulate few electron structures under consideration of atomistic effects. Many aspects make this work challenging, including preconditioning the Eigen problem and convergence coupling of the various program pieces, but our group has relevant experience to bring to bear on the problem.

Summary of Accomplishments:
We have made a great deal of progress in the first year of this project. We now have a workable Poisson semiclassical quantum dot simulation capability, and have been exploring the use of this capability with real geometries from our experimental modelers. This capability has also been integrated into Dakota software, allowing optimization of gate voltages to tune electron occupation of the quantum dot, tunnel barrier transparency, and proximity of charge sensing channels. We have begun the computation of Schrodinger-Poisson solutions and are exploring methods of iterating between the Schrodinger and Poisson steps.

Significance:
By marrying our expertise in quantum-electronic devices with our capabilities in classical device modeling and component-based code development, we have created a significant design capability for quantum-scaled electron devices. The capability is already impacting Sandia's ability to design and realize novel qubit structures for quantum computing and enables the design of novel sensors and devices based on nanowires and quantum dots. It also provides a valuable design tool for devices based on more aggressive nodes on the semiconductor roadmap.

Control and Optimization of Open Quantum Systems for Information Processing and Computer Security
151299

Year 1 of 3
Principal Investigator: M. Grace

Project Purpose:
Quantum information processing (QIP) holds the promise of radically altering computer science, particularly computer security and the simulation of quantum-mechanical systems. For example, there exists an efficient quantum algorithm that can break public-key cryptography schemes, which are based on the computational difficulty of prime factorization. By contrast, quantum cryptography guarantees secure communication based on physical laws, not computational difficulty. Consequently, security-related agencies worldwide are actively investigating this potential. However, significant obstacles exist, such as the effects of open-system dynamics (i.e., the unwanted coupling of a quantum computer (QC) to its environment), and uncertainties in the devices/controls that store or process information. Achieving the error threshold for fault-tolerant QIP is extremely difficult given device/control fluctuations, experimental constraints, and the unavoidable coupling of a QC to its environment. The report, "A Federal Vision for Quantum Information Sciences," establishes the importance of QIP in federally funded research and emphasizes the need to explore the fundamental limits of controlling quantum systems and to analyze the implications of these limits.

We are developing a crucial enabling technology with our academic collaborators, namely, the ability to control and explore processes at the quantum-mechanical level and assess the limits of control. This work will provide a tool to guide experimentalists and theoreticians toward creating practical QIP and general quantum devices. We will exploit the favorable "trap-free" structure of quantum control landscapes to generate families of high-fidelity controls that perform logical operations necessary for QIP. Advances in differential geometry will allow us to systematically search these families for controls that are robust, require minimal resources (e.g., energy, structure, time), and quantitatively probe limits imposed by the physical constraints of current technologies. Implementing these methods will yield exploration and optimization tools that can intelligently locate robust controls, if they exist, for practical quantum-mechanical objectives, thereby advancing Sandia's overall efforts at quantum device engineering.

Summary of Accomplishments:
This project includes several academic/industrial collaborations, with each addressing different aspects of quantum control and QIP, focusing on system/control robustness and minimal usage of resources. We mathematically and numerically explored the robust control of uncertain one- and two-qubit spin systems using three distinct approaches:

- Systematically combining recent advances from research in so-called "bang-bang" control with optimal control (OC) to design controls for quantum memory protocols.
- Developing an approach based on sequential convex optimization to design controls for general quantum operations, including robust qubit gates.
- Explicitly incorporating a measure of robustness into our OC formulation to design optimal robust controls.

Each approach produces high-fidelity controls, with individual benefits. Subsequent research will quantitatively compare the above approaches and characterize their relative merits.

Additionally, by exploring the underlying quantum-control landscape, we numerically generated minimal-energy and minimal-time OCs for noiseless multiqubit systems and robust OCs for qubit systems with noisy controls. Manuscripts presenting this work are in preparation. We have also developed flexible quantum-control protocols for trapped atoms/ions. In this context, we have completely characterized the topology of the quantum-control landscape, from state-to-state transitions to full operator control. Additionally, we have developed a mathematical functional to quantify the "entanglement" capacity of quantum operations through iterated optimization. Entanglement is a crucial property for QIP; consistently measuring the entangling power of operations is necessary to generate controls that produce this resource. Rather than previous state-based approaches, our functional uses quantum operations directly as inputs to compute entanglement capacity; this work is still in progress and properties of the entanglement measure are being fully characterized. Lastly, we have developed and tested methods — beyond conventional Monte Carlo methods — to simulate/control stochastic quantum systems.

Significance:
The resulting analysis and computational tools will be extremely useful to Sandia's entire quantum device engineering efforts. The publications resulting from this research will establish Sandia as a pioneer in quantum control and decoherence management.

This research project relates to the cyber security protection program of the DOE national security efforts, which calls for new technology to "preserve the integrity, reliability, availability, and confidentiality of important information." Because of the potential for QIP to radically alter the cyber security landscape, the results of this research could also affect the long-term aspects of the National Cyber Security Division of the DHS. In addition, applications to quantum sensing, a field that is being pursued by Defense Advanced Research Projects Agency, National Aeronautics and Space Administration, and National Institute of Standards and Technology, would also benefit from the results of this work.

Modeling Reactive Transport in Deformable Porous Media Using the Theory of Interacting Continua
152507

Year 1 of 2
Principal Investigator: D. Z. Turner

Project Purpose:
Recent reports illustrate growing international interest in using carbon-dioxide (CO_2) sequestration in geological formations to reduce greenhouse emissions. If implemented on the scale needed to make noticeable reductions in atmospheric CO_2, a billion metric tons or more must be sequestered annually (a 250-fold increase over today's amount). Unfortunately, existing simulation codes lack robust capabilities for modeling these problems. In addition, a number of other problems of critical interest to the DOE and Sandia, including long-time storage of nuclear waste, seepage of contaminants, pyrotechnics, and decomposing ablators on re-entry systems, allude to the paramount need for robust numerical methods for reactive transport in deformable porous media.

This research is guided by the following hypothesis: a treatment of reactive transport in deformable porous media using the Theory of Interacting Continua and from a differential algebraic equation (DAE) perspective, with an emphasis on stability, accuracy and efficiency, will enable tremendous capabilities for solving complex fluid-solid-chemical interaction problems of particular national interest. As compared to existing methods, which treat the underlying equations exclusively as ordinary differential equations (ODEs), we will employ numerical techniques from the DAE literature that respect the stability and order-of-accuracy of DAE solvers that are not addressed by standard ODE-based solvers. Furthermore, existing approaches for fluid-solid interaction (FSI) assume that the fluid and solid occupy separate distinct domains interacting only at a global-scale interface. This class of methods is not applicable for transport in deformable porous media because in these problems the fluid and solid essentially occupy the same domain (the flow occurs inside the void space of the solid). To address the coincident nature of these problems, we will use the Theory of Interacting Continua, which homogenizes both constituents, allowing them to co-occupy the domain occupied by the mixture. This approach will lead to broad application to a variety of important problems.

Summary of Accomplishments:
All of the stated first-year objectives have been met. In addition considerable crossover impact has been leveraged to benefit other Sandia efforts including a three-phase implementation of a thermodynamic model for carbon dioxide sequestration, algorithmic stability analysis for coupling flow and deformation in porous media, and improvements to SIERRA codes to enable mass balance and energy conservation for multiple species and phases.

To accurately capture the localized changes in permeability and displacement due to cracks, a nonlocal method was employed. The method has an integral-based governing equation that easily incorporates discontinuities. Using a state-based formulation, in a discrete sense, the solution is obtained by summing the force-states of all points within the horizon to obtain a balance of linear momentum. As the points are pushed away from each other by the pressure of the fluid in the porous media, the bonds between these representative particles are stretched. Cracks are incorporated as broken bonds between particles that form when the critical value of stretch is exceeded. Once the bonds for a particular particle begin to break, the percentage of broken bonds is treated as the damage for that point. This damage field is used to model changes in permeability.

Significance:
This work includes mission ties in carbon-dioxide capture and sequestration, storage of nuclear waste, enhanced oil recovery, seepage of contaminants (of interest to DOE's Office of Energy Efficiency and Renewable Energy), modeling of a variety of explosive and/or energetic devices (of interest to DHS), and design of decomposing ablators on re-entry systems or hypersonic cruise vehicles (of interest to DOE/NNSA, DoD, and the National Aeronautics and Space Administration).

Automated Exploration of the Mechanism of Elementary Reactions
153342

Year 1 of 2
Principal Investigator: J. Zador

Project Purpose:
Optimization of new transportation fuels and engine technologies requires characterization of the combustion chemistry of a wide range of fuel classes. Theoretical studies of elementary reactions — the building blocks of complex reaction mechanisms — are essential to accurately predict important combustion processes such as autoignition of biofuels. The current bottleneck for these calculations is a user-intensive exploration of the underlying potential energy surface (PES), which relies on the "chemical intuition" of the scientist to propose initial guesses for the relevant chemical configurations. For newly emerging fuels, this approach cripples the rate of progress because of the system size. Developing the necessary computational tools for an automated stationary point search that also interface to our already existing chemical kinetic tools will represent a quite useful advance that addresses the critical path on the development of key elementary reaction mechanisms necessary for the optimization of new fuels for the 21st century.

Published methods for automated identification of relevant chemical structures are computationally expensive due to their general nature. Also, these methods do not take advantage of the large body of chemical knowledge (i.e., the approximate structures that are relevant can be predicted or are known for the majority of the reactions). The problem that researchers in theoretical chemical kinetics often face is not the proposal of a new chemical pathway, but rather the actual execution of the related calculation, which currently requires much human interaction. The proposed algorithm incorporates a fundamental new approach by integrating chemical knowledge into the code and will significantly accelerate and almost completely automate the exploration of the possible pathways in elementary reactions relevant to combustion. Efficient exploration of these high-dimensional spaces involves significant algorithmic and computational challenges, requiring the combination of state-of-the-art tools of various research areas.

Summary of Accomplishments:
We have developed the chemical exploration module. The current program is able to interpret a chemical structure given in Cartesian coordinates (i.e., x, y, and z spatial coordinates of the atoms) in chemical terms, exactly as a human would do. The code "finds" the connectivity of the atoms, determines automatically whether it is a transition state or a stable species, a radical or a closed shell molecule, and whether it contains rings or not. The code also determines the unique torsional angles in the molecule and creates an interface to use the Gaussian09 quantum chemical package to explore the conformational energy landscape of the structures. The code is running these calculations in parallel, taking advantage of the computational cluster. The fitted 1D torsional scans can be directly inserted into our existing kinetics code. These advances already significantly reduce the amount of human time required to carry out calculations. The current program works for molecules containing C, H, and O atoms, which covers the requirements for applications in combustion, and it is currently in beta testing. We have implemented the first few test cases for finding transition states based on preexisting chemical knowledge, and the code performs according to our expectations. The first test case is the ROO ←→ QOOH transition state, which plays a significant role in autoignition chemistry. We also plan to implement transition states related to bond cleavage, by systematically lengthening the bonds and finding energetic maxima along this reaction coordinate.

As part of the code development we also consider the multidimensional exploration of the conformational space. Our code can currently fit such a surface and find all minima (4D, 28,256 points, ~80 minima).

Significance:
This project will advance the state-of-the-art in development of chemical models for complex hydrocarbon molecules, for example, in biofuels. This development will enable improved understanding of the oxidation of biofuels. Accordingly, this work benefits the energy security mission of DOE, by contributing to the development of effective biofuels and associated combustion processes.

Multiphysics Modeling of Environmentally Activated Network Polymers
153890

Year 1 of 2
Principal Investigator: K. N. Long

Project Purpose:
Environmentally activated polymers (EAP) exhibit complex mechanical behavior in response to external stimuli such as exposure to light at specified wavelengths or to temperature change within the material. Such environmental-mechanical couplings make possible smart EAP applications, including: 1) thermally removable encapsulation for electronics packaging, 2) photo-activated flaw mitigation in polymer structures, and 3) thermal or photo-mechanically activated self-deployable structures.

However, the state-of-the-art for most EAP systems relevant to laboratory objectives is limited to simple characterization and demonstration experiments, which is inadequate to describe their environmental-mechanical behaviors in sophisticated, application-oriented settings. Therefore, the critical scientific need to enable widespread use of EAPs is the development of theoretical and computational tools necessary to rapidly guide EAP design efforts.

This project endeavors to address that need by formulating mechanistically driven, continuum-scale, multiphysics material models that will be implemented into the SIERRA Mechanics finite element architecture for two EAPs activated by thermal and photo stimuli, respectively.

Continuum-scale, coupled multiphysics (thermal-chemistry, photochemistry, etc.) mechanical modeling of EAPs is a novel and enabling research topic. Although new EAPs are developed regularly, few theoretical/computational efforts in the literature connect the underlying physics to the macroscopic mechanical behavior of such systems as we are doing. Such efforts will enable accelerated design and application development with two EAPs, activated by temperature change and light, respectively. Our approach involves a flexible, plug-and-play framework to model the physics for different EAPs. This framework allows for integration of supportive multiscale calculations and experimental data to determine specific environmentally stimulated chemical and microstructural evolution rules. Successful implementation of this flexible approach will accelerate modeling efforts of future EAPs at Sandia. Significant challenges include the following: developing a robust theory, implementing coupled physics, calibrating specific material models to experimental data, and validating model performance against complex photo/thermal-mechanical boundary value problems.

Summary of Accomplishments:
Photomechanical buckling experiments were performed at the University of Colorado, Boulder (CU-B) with our collaborators, which we predicted using our photo-mechanical constitutive model that is implemented into an ABAQUS (finite-element computer code) UMAT (user material). These experiments and predictions demonstrate an enormous design space in the use of photomechanical buckling of polymer films for sensing and actuation.

Experiments were performed on unaixially extended, photopatterned films to produce controllable trenches and ridges potentially useful for lab-on-chip and microfluidics purposes. We have analytical and finite element models to accompany this work, but thus far, experimental measurements and analytical/computational predictions are not in good agreement.

We completed the development and implemented into an ABAQUS UMAT, a phenomenological model to efficiently account for the simultaneous deformation and microstructural evolution of material point. The method is particularly applicable to polymers that experience bond exchange and network scission and healing mechanisms. Colleagues at CU-B are completing this work.

We adapted the modeling efforts towards modeling the equilibrium behavior polymer networks undergoing scission and reformation due to a Diels-Alder reaction of side-chain or in-chain functionalities. The approach is thermodynamically admissible in a continuum thermodynamics setting and broadly applicable to other environmentally activated materials. Specifically, the Diels-Alder functionalized polymer was developed at Sandia and is currently in use, but no model exists to describe its thermal-chemical-mechanical behavior.

Significance:
The ability to control a large deformation response via user-specified environmental stimuli offers unique material capabilities useful to national security interests and the maintenance of nuclear arms. Specifically, EAPs are candidates for novel biosensors, self-deployable structures for aerospace applications, and encapsulation materials because they can be (locally) nondestructively repaired and/or removed/replaced for the servicing of on-board electronics. The latter application has potential implications to simplify the maintenance of the stockpile since such materials self-heal and can be reused rather than remade.

Refereed Communications:
K.N. Long, T.F. Scott, M.L. Dunn, and H. J. Qi, "Photo-Induced Deformation of Active Polymer Films: Single Spot Irradiation," *International Journal of Solids and Structures*, vol. 48, pp. 2089-2101, March 2011.

Combinatorial Optimization with Demands
154002

Year 1 of 2
Principal Investigator: O. D. Parekh

Project Purpose:
In many practical discrete optimization and resource allocation scenarios, commodities such as bandwidth are discounted when purchased in bulk, and piping and cabling may only be available in a small number of types of varying capacity and cost. Such scenarios result in a nonlinear relationship between cost and capacity, which may be modeled infusing traditional combinatorial optimization models with a feature called demands. Thus the challenge is to design algorithms for models endowed with demands while leveraging the rich and immense mathematical infrastructure developed for traditional linear and discrete optimization. Even without considering economies of scale or demands, most of the underlying problems we consider are already nondeterministic polynomial (NP)-hard; a means of mitigating this is designing an approximation algorithm, an efficient heuristic algorithm that provably produces a high quality solution.

We will develop approximation algorithms for resource allocation problems that exhibit economies of scale and are modeled using demands. We aim to accomplish this by generalizing a celebrated technique called iterated rounding that has been instrumental in resolving several open problems since its inception late last decade. While iterated rounding is difficult to adapt to the types of resource allocation problems we consider, even without economies of scale, our method is designed to handle these hurdles while retaining many of the elegant properties of iterated rounding. In addition we seek to unearth deeper connections between well-understood discrete optimization problems and their significantly more complex demand-endowed counterparts. We expect that such insights will generally help us better understand and model the latter, which are frequently encountered in different application-oriented contexts at Sandia. A particularly powerful feature of our proposed method is that it implicitly produces a diverse collection of near optimal solutions, which is useful for uncertain or multiple objective functions.

Summary of Accomplishments:
Resource allocation problems are ubiquitous in applications of national interest. The overarching goal of this project was to develop higher quality algorithms for classes of resource allocation problems whose difficulty results from economies of scale. These problems are provably hard to solve to optimality, hence our focus was on efficient algorithms which deliver approximately optimal solutions along with a guarantee bounding the worst case quality of a generated solution relative to an (unknown) optimal solution. Our major accomplishment has been the design of an algorithm that is guaranteed to always efficiently produce a solution whose quality deviates from optimality by a factor of at most 2k, (where k is a parameter related to the sparsity of the problem instance). Prior to our work, the best-known algorithm delivered a guarantee of 8k. Moreover, we were able to show that improving our result would be very difficult, if not impossible, lending evidence that our findings are the “correct answer.” This work was presented at the prestigious peer-reviewed *Integer Programming and Combinatorial Optimization* conference in June 2011 and published in its proceedings. More recently, we have been productive in developing improved algorithms for network design problems, and some of our work has been submitted for publication in a journal while a paper outlining the remainder is currently in preparation.

Significance:
Resource allocation problems are abundant in applications of national interest, and more accurately modeling economies of scale could have an impact on national security missions and applications such as scheduling for the Pantex Plant, DOE/NNSA Office of Secure Transportation, Federal Aviation Administration, integrated stockpile evaluation, and future combat systems; routing for massively parallel processing; sensor placement for Environmental Protection Agency water security; and graph generation for cyber security and nonproliferation.

Refereed Communications:
O.D. Parekh, "Iterative Packing for Demand and Hypergraph Matching," in *Proceedings of the 15th Conference on Integer Programming and Combinatorial Optimization (IPCO),* 2011.

Improved Performance and Robustness of Scalable Quantum Computing
154059

Year 1 of 2
Principal Investigator: C. Brif

Project Purpose:
Quantum information science and technology (QIST) hold the promise of revolutionizing computer science and physics. Of particular importance is the potential capability of a quantum computer (QC) to efficiently solve problems which are believed to be intractable on a classical computer. The potential impact of QIST on national security is widely recognized, and sizable efforts are focused on this research. However, significant outstanding challenges exist, such as implementation of scalable quantum computing systems. While few-qubit operations have been demonstrated, realization of a scalable multiqubit QC has proven elusive. At the heart of this challenge is the problem of robustness of QCs to control noise. External controls are necessary to enact quantum logic operations, and inevitable control fluctuations result in gate errors in realistic QCs. Characterizing the control noise effect on the QC performance and developing robust control strategies for scalable multiqubit architectures are crucial for advancement of practical quantum computing.

The purpose of the project is to develop powerful analytical methods and numerical optimization tools necessary for exploring and enhancing the robustness of realistic multiqubit QCs to control noise. A critical question explored in the project is how the noise-induced errors scale with the QC size in the presence of unwanted inter-qubit couplings. In order to perform the robustness analysis, the project utilizes properties of the quantum control landscape that relate the physical objective (the quantum computation fidelity) to the applied controls. The objective is to identify optimal controls with enhanced robustness by using two complementary approaches: 1) landscape characterization in the vicinity of the optimal control manifold, and 2) multi-objective optimization that explicitly incorporates the requirement of high robustness.

Summary of Accomplishments:
In FY 2011, we formulated the problem of robust control of quantum gates in the presence of noise and expressed the dependence of the quantum gate fidelity on noise characteristics. Specifically, we demonstrated that the gate error due to small, random noise in an optimal control field is given by the overlap of the control's Hessian with the noise autocorrelation function (in time domain) or with the noise power spectral density (in frequency domain). This formalism provides the capability to evaluate the gate error for any given stochastic noise model. In particular, for additive white noise (AWN), we computed the overlap analytically and discovered that the gate error is proportional to the noise variance, dipole square norm, and control time. This analysis shows that maximizing the robustness to AWN is equivalent to minimizing the control time. Since the minimal control time is determined by the requirement of keeping the system controllable, this result establishes a direct relationship between controllability and robustness of quantum computing systems. This result also helps us to explore how errors induced by AWN in multiqubit gates and quantum circuits scale with respect to the number of qubits. To this end, we employ both analytical (Lie-group-theoretic) and numerical methods to determine the scaling of the minimal controllability time with respect to the number of qubits for various types of inter-qubit couplings (this line of research is currently in progress). For non-white noise, we discovered that the dependence of the gate error on the control time rapidly decreases as the characteristic noise correlation time increases. This effect indicates the possibility of identifying optimal control fields with maximum robustness to non-white noise with a given spectrum. We explored the

search space structure and found that the robustness optimization can be facilitated by using a combination of stochastic and gradient-based algorithms.

Significance:

The research objectives of the project are strongly related to the cyber security protection program of the DOE national security efforts, which call for new technology to "preserve the integrity, reliability, availability, and confidentiality of important information." Quantum computing has the potential to radically alter the character of cyber security problems, which makes the results of the project highly relevant to the long-term aspects of the National Cyber Security Division of the DHS. The project addresses some of the most critical challenges facing the development of scalable quantum computers and thus is likely to have a significant impact on both fundamental and practical aspects of quantum information science and technology. In addition, the developed methods of noise mitigation may find applications in quantum sensing, a related field which is being pursued by Defense Advanced Research Projects Agency, National Aeronautics and Space Administration, and National Institute of Standards and Technology.

A Geometrically Explicit Approach to Adaptive Remeshing for Robust Fracture Evolution Modeling
154317

Year 1 of 2
Principal Investigator: M. Veilleux

Project Purpose:
The purpose of this project is to develop a high fidelity, geometrically accurate approach to modeling fracture. All weapons systems exposed to hostile/abnormal environments are subject to failure. A common concern is whether an exclusion region will be breached under abnormal mechanical loadings, such as a drop or transportation accident. These issues necessarily involve fracture. However, analysts cannot determine the root cause of failure, or uncertainty thereof, using common modeling approaches. Such approaches typically reduce model complexity at the cost of physical fidelity by smearing crack behavior or limiting crack locations to mesh dependent paths.

Here, we seek to model the cause and uncertainty of failure by explicitly representing fracture (i.e., arbitrarily non-planar evolution of geometrical facets [fracture surfaces]) driven by non-uniform load distribution and resisted by heterogeneous material toughness. The primary focus is on accurate geometrical representation of fracture through local topology and mesh adaptation. However, to facilitate accurate physical representation, other challenges are also addressed (e.g., material bifurcation; non-local regularization; and remapping of history-dependent material states).

Although geometrically explicit fracture representation has been commonplace for over twenty years, computational and algorithmic demands have stalled extension of such approaches to complex crack evolution processes. Adaptive crack insertion and propagation routines are not available in current production codes, both internal and external to Sandia, and such routines in external research codes are generally limited to linear elastic fracture mechanics and well-behaved elastic-plastic fracture mechanics applications that rely on criteria and do not model failure process evolution.

The principal investigator combines his knowledge in adaptive crack modeling, meshing with the high performance computational capabilities at Sandia, to bring to fruition the extensive rewards of geometrically explicit modeling of arbitrarily non-uniform fracture evolution. The approach is applicable for multiple length scales and fracture mechanisms, but, for proof-of-concept, this study focuses on representing macro-scale ductile fracture.

Summary of Accomplishments:
In FY 2011, we demonstrated the ability to geometrically model evolving cracks in Sandia's finite element modeling codes. While accomplishing this goal, we achieved the following project outcomes:

- We demonstrated the ability to create the geometries of nucleated and propagated cracks through a coupling of FRANC3D (geometric fracture representation software) with Exodus (Sandia's finite element analysis database).
    - We updated the FRANC3D source code to read/write Exodus files.
    - We demonstrated success by generating a 3D crack geometry in a finite element model of a test specimen.

- We remeshed a model upon crack geometry adaptation and demonstrated that this mesh is sufficient for analysis in Sandia's finite element analysis codes (SIERRA and LCM):

- We demonstrated the ability to remesh with tetrahedral finite elements around an inserted/propagated crack in FRANC3D.
- We proved that linear tetrahedron formulations near a crack were insufficient for finite element solver convergence.
- We proved that generation of hexahedral finite elements was currently impossible for arbitrary crack geometries.
- We demonstrated the ability to output quadratic tetrahedral meshes and to compute converged finite element solutions for models with propagating cracks.
- We implemented a semi-automated, Python program that interfaces between FRANC3D and SIERRA/LCM. The result is a command-line driven tool for accurately representing cracks in locations and directions determined by physical criteria.

Significance:
For the science and technology community, this research project will result in a fracture modeling approach that reduces the dependence of crack paths on the numerics. Researchers and analysts can greatly improve predictions of crack locations and shapes, because the physics governing crack propagation, which know nothing about the numerics, can be discovered and applied more effectively and accurately, and the crack locations and their typically complex shapes can be accurately represented. It also leverages ongoing research in the fracture community. For example, regularization methods, such as cohesive zone models and strain localization models, can utilize the tools produced by this project to adaptively insert surface elements, which encompass these regularization methods, along a physically predicted crack path.

This work is intended to benefit the DOE national security mission to ensure the safety and integrity of the country's nuclear weapons, within the focus area of scientific discovery and innovation. Geometrically explicit representation of fracture processes is a novel approach at Sandia that enables high-fidelity simulation of damage of weapons upon drops or other accidents. Such simulations increase the ability to evaluate safety of current weapon encasements and facilitate the design of more fracture-resistant systems without full-scale tests.

Clustered Void Growth in Ductile Metals
154568

Year 1 of 2
Principal Investigator: T. D. Kostka

Project Purpose:
Since ductile metals generally fail though the nucleation, growth, and coalescence of voids, it is essential that we understand this phenomenon in order to better predict failure in these materials.

Using a developed research code, we are examining the problem of clustered void growth in ductile metals by investigating and identifying important microstructural configurations and attributes that accelerate or delay the formation and growth of voids and macroscopic material failure. In parallel to this, we wish to have these capabilities implemented into the SIERRA implicit dynamics code, Adagio. The first year of this project is focused on researching clustered void growth with current capabilities and implementing the HEX20 element and a far-field traction-based boundary condition into SIERRA.

In the second year, we will be able to validate the implemented features against analytical solutions and a current research code. We will then transition away from the research code and explore clustered void growth for much larger problems by using parallel processing capabilities of SIERRA.

We will be creating a deeper understanding of clustered void growth under varying triaxiality which will be instrumental in creating new void growth and predictive failure models. These results will be contrasted against those of dilute void growth to show the similarities and limitations of the dilute assumption.

Running large-scale, representative three-dimensional clustered void growth simulations will put us at the forefront of modeling fracture surface.

Summary of Accomplishments:
We have: 1) developed a randomized microstructure generation capability to model a periodic configuration of voids representative of those found in structural metals, 2) developed an automated mesh generation capability, 3) developed a linear constraint system to enforce periodic boundary conditions in a non-symmetric body without over-constraining the geometry, and 4) identified, from literature, microstructural parameters representative of our material of interest, 304L stainless steel, for use in these simulations.

Using these tools, we have run many sets of simulations to characterize the softening curve associated with void growth and coalescence. The results from this have shown a large spread in results from which we characterize the distribution of the failure strain of the material for a given set of microstructure generation parameters.

We have also shown the efficiency of the HEX20 element in comparison to its linear counterparts in large-scale plasticity problems. We have also proven the performance of two selective deviatoric formulations for problem in which the triaxiality or pressure field is of interest, including selective integration techniques.

Significance:
The results from this project fit into DOE's theme of scientific discovery and innovation. In particular, we will contribute state of the art advances in computational sciences and add to the understanding of void growth and failure in ductile metals. Both of these contributions will add to our knowledge in the realm of material failure and add confidence to our capabilities and results in this area.

The ability to model ductile fracture is of critical importance to Sandia's mission to ensure the safety and reliability of the US nuclear weapon stockpile. The results of this work will aid in the development of advanced void growth laws for use in modeling fracture of ductile metals to support Sandia's mission.

Interface-Tracking Hydrodynamic Model for Droplet Electrocoalescence
155327

Year 1 of 3
Principal Investigator: L. C. Erickson

Project Purpose:
Many fluid-based technologies rely on electrical fields to control the motion of droplets (e.g., microfluidic devices for high-speed sorting of water droplets in oil or for purifying biodiesel fuel). Precise control over droplets is crucial for these applications. However, electric fields can induce complex and unpredictable fluid dynamics. For example, oppositely charged water drops immersed in silicon oil experience attractive forces that would favor their coalescence. Recent experiments with high-speed cameras demonstrate the counterintuitive behavior that these oppositely charged droplets bounce rather than coalesce in the presence of strong electric fields. A transient aqueous bridge forms between approaching drops prior to pinch-off. This observation applies to many types of fluids, but neither theory nor experiments have been able to offer a satisfactory explanation. Analytic hydrodynamic approximations for interfaces become invalid near coalescence; therefore, detailed numerical simulations are necessary. This is a computationally challenging problem that involves tracking a moving interface and solving complex multiphysics and multiscale dynamics, which are beyond the capabilities of present simulations. An interface-tracking model for electrocoalescence can provide a new perspective to a variety of applications in which interfacial physics are coupled with electrodynamics, including electroosmosis, fabrication of microelectronics, fuel atomization, oil dehydration, nuclear waste reprocessing, and solution separation for chemical detectors.

Accurate and stable interface-tracking methods capable of capturing and predicting coalescence and break -up of interfaces are currently a major challenge in the computational science community. Including electric forces poses a further challenge due to the complexity of electrostatic and hydrodynamic interactions involved in coalescence, requiring a novel modeling approach to understand this phenomenon. This project will entail the creation of an interface-tracking model using the advantages of the conformal decomposition finite element method (CDFEM) with the capability to reproduce experiments, make predictions for future experiments, and answer questions about the physics of this phenomenon that are not experimentally accessible.

Summary of Accomplishments:
We designed a test problem to examine the advantages and disadvantages of a variety of interface-tracking methods using Aria. The test problem chosen was a water droplet immersed in oil suspended above a water surface that impacts the water surface due to a gravitational force. The numerical methods implemented and examined thus far include a diffuse level set method, arbitrary Lagrangian-Eulerian (ALE) moving mesh method, and CDFEM.

We studied this area and determined the appropriate set of equations that describe the behavior of the electric field necessary for the coalescence model. We also learned how to add these changes in the SIERRA/Aria code environment and examined Aria's current capabilities to determine what new code changes need to be implemented in order to run the full model. Aria did not handle coupling between fluid velocity and an electric field, so we included a Maxwell stress tensor into the Navier-Stokes equations, effectively coupling the electric field (voltage) equation to the fluid equations. We have also verified that this implementation is correct by creating and testing simple problems with analytic solutions. We added a new equation to Aria that describes the evolution of charge density in the model, since this feature was not yet available. The charge density equation is now coupled to the voltage equation which determines the electric field that the fluids are exposed to in order to obtain the full model for droplet electrocoalescence. Lastly, we tested the full model's capacity with CDFEM on a test problem of sharp interface drop deformation due to an electric field to ensure that the jump conditions for the Maxwell stress tensor were properly satisfied. This test problem appears to match similar experiments and numerical experiments quite well.

Significance:
An interface-tracking model for electrocoalescence can provide a new perspective to a variety of applications in which interfacial physics are coupled with electrodynamics, including bubble formation, electroosmosis, fabrication of microelectronics, fuel atomization, oil dehydration, nuclear waste reprocessing, and solution separation for chemical detectors. This model could improve methods for purifying biodiesel fuel by guiding future designs through analysis to efficiently remove excess alcohol and other contaminates using electric fields. Comparison between models and direct experimental observations will aid in validation and verification (V&V) for interface-tracking methods. This project expands Sandia's computational capabilities for this important class of applications.

Automated Generation of Spatially Varying Stochastic Expansions for Embedded Uncertainty Quantification
155551

Year 1 of 3
Principal Investigator: E. C. Cyr

Project Purpose:
Uncertainty quantification (UQ) is increasingly recognized as necessary to assess the effect of variability of input parameters on a physical model. For phenomena described by systems of partial differential equations (PDEs), the variability is derived from coefficients, boundary conditions, or forcing terms, which are all modeled by a random variable with a particular distribution or a range of possible values. The result is a PDE that has a stochastic solution that reflects the variation in the input.

Current UQ methods, like stochastic collocation or Monte-Carlo sampling, approximate the stochastic solution by treating the required resolution of the uncertainty as uniform across the physical domain. To understand the consequence of this, consider a convection-dominated flow where uncertainty is injected at a point in the domain. Only the solution downstream of the injection point will be affected by the uncertainty. The upstream solution will be fully defined by the deterministic PDE. Modern UQ methods would resolve both the upstream and downstream solutions with the same resolution. But this wastes computational resources on the upstream solution and may under-resolve the solution downstream. For more realistic multiphysics applications that are characterized by a range of time and spatial scales, the required degree of resolution of the stochastic solution across the physical domain is an open question.

The purpose of this project is to develop methods that efficiently and accurately construct a spatially varying stochastic expansion. Our approach uses embedded UQ technology to construct the expansion using adjoint-based error estimation and refinement. The potential benefit is two-fold. First, any investigation into the spatially varying resolution requirements of the stochastic solution represents novel research that will shed light on the nature of uncertainty in PDE systems. Second, an adaptive refinement algorithm would better utilize computational resources enabling simulation of larger, more complex physical systems, revealing greater insights into more challenging physics.

Summary of Accomplishments:
In FY 2011, this project laid the foundation for future work applying the spatially varying technology to more complex physics. This involved a substantial early development phase where the spatially varying discretization was implemented in the Stokhos package (part of the Trilinos framework). While this implementation is not yet fully realized, it is already a one-of-a-kind technology that will serve as the primary research and development vehicle in the next phases of this project.

Studies on the use of a spatially varying discretization for a model 1D convection diffusion problem were also undertaken during FY 2011. This included a preliminary study using existing embedded UQ techniques that demonstrated that the required resolution of the stochastic expansion has a strong spatial dependence for this model problem. This is particularly true for parameterizations leading to problems that are primarily convected. We also considered the effect of choosing a fixed spatially varying expansion for this problem (high order stochastic discretization in one region of the physical domain and low order in another). For more convected problems, the spatially varying discretization performed well, matching the solution with minimal error. However, for more diffusive systems the spatially varying discretization suffered. Further studies with an adaptive refinement strategy based on computing the residual of the fully resolved problem were also performed. While this algorithm is certainly suboptimal, these result show that the adaptively generated spatially varying discretizations can achieve high accuracy with fewer unknowns than a standard uniform-in-space discretization.

Significance:
Development of embedded enhanced UQ capability enables simulation of more complex physics with greater confidence in the results. This project has the potential to have strong impacts on the DOE mission space. UQ in computational modeling for the Nuclear Weapons (NW) community is a preeminent issue when the analysis is used for weapons system qualification for life extension programs, as well as for the annual assessment. Additionally, engineering analysis problems involving multiphysics systems, like those defining energy and climate models, benefit from UQ approaches.

The research done by this project has shown the benefit of spatially varying UQ to a primarily convected one-dimensional PDE. While simplistic, this PDE is representative in that it has spatially localized features similar to those that would be expected in a multiphysics application. Successful application of the techniques developed by this project to these problems would potentially enable higher fidelity UQ simulations at a lower computational cost.

One potential target application of relevance to the nuclear weapons community is in semiconductor modeling. Already, UQ is used as part of the QASPR effort to certify electronic systems for intense radiation bursts. The set of PDEs used to model the semiconductor devices can be considered a convection-diffusion-reaction system similar, though vastly more complex, to the 1D convection-diffusion PDE already studied by this project. If the results of the refinement studies conducted in this fiscal year were to extend to the more complex physics, then the potential reduction of work in a spatially adaptive UQ approximation could be substantial without affecting accuracy. This would allow for higher-fidelity simulation of more complex devices, all while maintaining the ability to assess the uncertainty propagated from unknown parameters.

Softening Behavior of Post-Damage Quasi-Brittle Porous Materials
155798

Year 1 of 3
Principal Investigator: T. J. Fuller

Project Purpose:
The state-of-the-art in structural failure modeling enables assessment of crack initiation and propagation, and progression to tearing, in many materials. Vulnerability assessments, as well as other applications (i.e., ceramic component manufacturing), suggest a need to track material behavior through failure to the point of fragmentation and beyond. This field of research is made particularly challenging for structures made of porous quasibrittle materials such as concrete, ceramics, rock, etc. These structures, when excessively loaded, will damage, soften, and eventually fail according to physical processes operating at comparatively large timescales in comparison to the initiating event. This project will develop constitutive models and associated numerical techniques suitable for capturing quasistatic softening, with experimental validation. This will be performed within the SIERRA Mechanics framework, but will be extensible to other formats.

The core of this research is the development of a softening model applicable to quasistatic loading that couples the constitutive response with that of the host finite element code by "shedding" load from highly stressed elements to adjacent elements such that equilibrium is maintained at each load step, as required by the implicit solvers used in quasistatic analysis. The proposed stress-shedding scheme has previously been attempted with some success in applications involving the softening of ductile materials, but has never been adapted to brittle materials. This method also differs from softening methods employed in explicit dynamic calculations, in which softening is allowed to progress without respect to equilibrium. The challenge lies in the transition from an initial high-rate transient damage event (blast or impact) to more slowly evolving damage occurring over much longer timescales of interest in geomechanical analysis. Although this capability is potentially useful to many applications, it arises from a growing interest in blast- and impact-induced damage associated with homeland security applications, as well as engineered subsurface reservoirs supporting future energy security.

Summary of Accomplishments:
Three key objectives toward the successful completion of the technical goals and milestones associated with this research project have been accomplished. First, the Kayenta material model has been integrated in the SIERRA Mechanics framework. Currently, a suite of nearly three-dozen validation and verification (V&V) problems is being ported from our standalone single-element material model development code to SIERRA. When each test is successfully ported and passed, Kayenta will be pushed into SIERRA's main development repository.

Second, we fit Kayenta's nearly 25 elastic and strength parameters to experimental data acquired from quasistatic triaxial compression/extension of Berea sandstone. Up to the peak load, the data show a high degree of nonlinearity and beyond the peak load strong localization and material softening until ultimate failure. Attempts were made to fit Kayenta to the softening portion of the experimental data. As expected, the effort was unsuccessful due to the softening scheme employed by Kayenta, developed in accordance with observations made during transient dynamic loading, not being capable of reproducing the material response observed during quasistatic loading. Accordingly, we developed and integrated three new softening models in Kayenta, each more capable of fitting data from quasistatic loading than the original. We are currently performing V&V tasks on each of the new softening models.

Lastly, we developed a novel standalone finite element material model driver designed for rapid development and testing of material models. Building on our experience working with the material model drivers, and incorporating feedback from several other material modelers, we developed a robust set of tools capable of exercising material models in ways not previously possible with existing tools. The new tool is proving invaluable in the development of the new softening models necessary for successful completion of this project.

Significance:
Predicting the deformation and failure of quasibrittle media through finite element simulations is a key component of a broad range of applications of interest to the DOE and national security. Successful outcome of this research will enable simulation of a broad class of problems ranging from those dealing with vulnerability of infrastructure (e.g., evaluation of hardness of concrete structures to insult, collapse of concrete structures, etc.) for the DoD to those addressing the integrity of the underground (mine collapse, underground storage seal integrity, defeat of hardened targets, etc.).

New Methods of Uncertainty Quantification for Mixed Discrete-Continuous Variable Models
156158

Year 1 of 3
Principal Investigator: L. E. Bauman

Project Purpose:
The scale and complexity of problems such as designing power grids or planning for climate change is growing rapidly, driving the development of complicated computer models that incorporate both continuous and discrete data. Both the models and the data are uncertain. Uncertainty quantification (UQ) provides the underpinnings necessary to establish confidence in these models and their use to support risk-informed decision-making. However, there are only a few approaches for mixed discrete-continuous variable models, and these become obsolete when there are multiple discrete variables or when the discrete variables are completely nonnumeric. Therefore, researchers focus on the uncertainty in their particular problem; thereby taking advantage of symmetries, simplifications, or structures. For example, uncertainty propagation in certain dynamical systems can be efficiently carried out after various decomposition steps. By combining some ideas from statistical genetics and computer experiments, we are developing a new method for performing UQ for mixed discrete-continuous models. We are focusing on two general classes of problems: moderate-scale problems with a modest number of discrete variables and large-scale problems where the discrete parameter space may be larger than the continuous one.

In classical biometrics when heritabilities are estimated, the aggregate effects of unobserved discrete genotypes are modeled as additive, continuous random variables. In computer experiments, one approach is to treat the deterministic output of a simulator as the sum of a fixed function and a random process. We will combine these approaches to create a new way to treat discrete variables in mixed variable problems. The key concept is to aggregate and transform the discrete variables into a continuous probabilistic variable, also leading to potential new capabilities for handling high dimensions. This method will provide a new tool for UQ, which is focused on efficient estimation of the cumulative distribution function (CDF) of possible output function values given the uncertain input values.

Summary of Accomplishments:
We are defining baseline capabilities for simple mixed-variable functions and some benchmark mixed-variable optimization problems as well as three problems in the model choices category. Initial results from the simple functions show poor performance: the variance is greatly reduced and the tails of the distribution are much shorter. These results do give some guidance about how many discrete variables would be needed for this method. They also demonstrate the effects of averaging over results; we will be addressing these concerns as we continue.

The first model choice problem concerns a contaminated groundwater site. The simulator models flow in the aquifer and assess the goal of zero contaminant flux across boundaries. Six wells are arranged in three scenarios: a six-variable scenario that sets the pumping rate for each well, a 12-variable scenario which adds a discrete on/off variable for each well, and a 24-variable scenario which adds x and y coordinates for each well. The discrete variables are wedded to the continuous ones. The discrete model choices empirical probability distribution function will actually summarize both the distributions of on/off indicators and pumping rates; then, wells will be placed according to some distribution. These two inputs create the output CDF.

The second problem stems from verification of a detailed physics model. One way to quantify the simulation uncertainty is to estimate the output CDF while varying the 17 input parameters that control the numerical analysis. Simulator results should exhibit very little variation due to changes in these parameters, and the CDF gives a measure of uncertainty due to numerical error.

The third model choice problem is also a detailed physics model where we have created a collaborative DART workbench project. A cylinder is randomly chopped up into blocks, different materials are assigned to each block, and the composite is heated.

Significance:
This work will give us the ability to include quantifying uncertainty of the effects of multiple discrete variables. For example, we continue efforts to perform verification and validation for models of stockpile stewardship. Second, the DHS describes 13 critical infrastructure sectors. In each of these areas, researchers are modeling systems to understand their function, improve efficiency, and plan for the future and for security. The ability to make UQ easier and more tractable will provide these researchers with tools for both understanding how uncertainties propagate through their systems, and for finding solutions which are robust to uncertainties.

Developing Highly Scalable Fluid Solvers for Enabling Multiphysics Simulation
156251

Year 1 of 3
Principal Investigator: J. Clausen

Project Purpose:
Computing hardware is trending towards distributed, massively parallel architectures in order to achieve high computational throughput. For example, Cielo will use 43,104 cores and Intrepid at Argonne National Laboratory uses 163,840 cores. Next-generation machines will continue this trend, with Sequoia at Lawrence Livermore National Laboratory using 1.6 million cores. This project will develop a fluid simulation algorithm based on artificial compressibility (AC) that is capable of scaling on massively parallel (exascale) architectures.

Traditional incompressible-flow solvers are based on the incompressible Navier-Stokes (NS) equations, in which the continuity equation acts as a constraint imposing a divergence-free velocity field. In this case, no direct coupling of pressure to velocity exists requiring an implicit solution. The fully coupled finite-element (FE) schemes currently used at Sandia scale to only O(100) processor cores. As an alternative, fractional step (FS) methods such as the popular pressure correction method gain some scalability; however, they must still solve a Poisson equation for the pressure field, which creates a high communication load between processors resulting in poor scalability at O(10,000) processors. An explicit FE method based on AC will allow for a local update procedure resulting in excellent scalability on O(100,000) processors; however, as originally formulated, the AC method shows transient errors that must be addressed. The solution uses a recently derived reformulation of the NS equations to eliminate these errors while retaining an explicit formulation.

Despite the uncertainties, the benefits of a scalable fluid solver will impact several areas at Sandia. This impact is most important in problems where high temporal resolution is required, for example suspension and emulsion flows, thermal convective flows, melt flows, and fluid–structure interaction. If successful, this project will deliver a fluid solver capable of scaling with Sandia's increasingly parallel computational resources.

Summary of Accomplishments:
We have implemented the constant-density kinetically reduced local Navier-Stokes (KRLNS) equations in the framework of SIERRA/TF. This required significant effort to allow explicit equation updates within the SIERRA/TF codes. Anomalous behavior was noted in the results. In order to differentiate between deficiencies in the discretization method or algorithm, we designed a research finite difference (FD) test code, which has several important benefits. First, algorithmic variations can be rapidly prototyped, and second, it allows a direct comparison to an already published algorithm using KRLNS. To provide further comparison, we have implemented two other previously published explicit methods: a traditional AC method and a lattice-Boltzmann method (LBM).

The FD test code shows that the published KRLNS method is overly dissipative, and performs poorly. Analysis of the existing derivation suggests an error with a term involving the dissipation of kinetic energy. It is not clear how the authors obtained the published results, and we are in the process of communicating with them about this issue.

Using the same scaling arguments from the KRLNS method (i.e., looking at the compressible Navier-Stokes at acoustic scales and assuming that fluctuation in temperature drives changes in pressure), an alternate form for the evolution of pressure can be derived from the entropy conservation equation without the obfuscation of using the grand potential. This method contains a smoothing term similar to that in the KRLNS method; however, proper dissipation rates are recovered in simulations of a decaying Taylor-Green vortex. We hope that this form of an AC equation can be combined in a novel fashion with other techniques such as dual time and multitime stepping to improve performance.

Significance:
Advanced fluid simulation capabilities are integral to maintaining the viability and safety of the nuclear weapons stockpile. The highly scalable methods herein are required to leverage the increasingly parallel computational platforms used by Sandia and the NNSA in pursuit of this mission.

Simulation of Primary Fuel Atomization Processes at Subcritical Pressures
156703

Year 1 of 3
Principal Investigator: M. Arienti

Project Purpose:
New biofuel formulations and modifications in engine design toward high efficiency and low emissions require better predictive computational capabilities — a need Sandia has responded to with increasingly sophisticated combustion codes. However, the distribution of fuel spray near injection must provide the correct boundary conditions to these codes. Direct observation of fuel atomization is difficult: nozzles are typically about a millimeter long and a fraction of a millimeter in diameter, and the flow moves at speeds on the order of several hundred meters per second. The fact that the fuel can partially vaporize in the nozzle adds another level of complexity. Overall, the understanding of the physics that controls the fuel/air distribution of many combustion devices, particularly at high pressure, is quite limited.

This project explores the fuel subcritical behavior (in temperature) in the liquid core and dense spray regions. It will be numerical in nature and provide an improved understanding of the early stages of fuel atomization (primary atomization), as well as the capability to guide future experiments and diagnostics development. Currently, external (with respect to the injection nozzle) simulations of primary atomization can be carried out with simplified inlet conditions. Conversely, internal flow calculations with vapor bubbles formation and flow separation are stopped at the nozzle orifice. The innovative element of this project is in allowing the coexistence of liquid, vapor, and gas in the same multiscale calculation of high-pressure flow. The coupling between orifice and external flow will be crucial in capturing the pressure feedback from the combustion chamber to the fuel nozzle, and, because of the high nonlinearity of combustion, it will substantially improve the predictive power of engine simulations.

Summary of Accomplishments:
The effort has been focused on validation of the existing interface capturing capability and on testing a new embedded boundary capability.

- Validation Milestone: A grid convergence and validation study demonstrated the capability of the multiphase flow solver CLSVOF (Combined Level Set Volume of Fluid) to correctly calculate spray size distribution without previous model calibration. The simulation configuration consisted of two water jets impinging on each other and exactly replicated the conditions of a published experimental study on small-thrust rocket engines. The validation results were submitted for publication to the *Journal of Propulsion and Power*. This test is a major step toward the objective of validating the spray characteristics associated to a realistic diesel injector at subcritical conditions. Since then, a synthetic turbulent inlet boundary condition based on a model of isotropic or sheared spectral tensor has been implemented.
- Algorithm Development Milestone: in parallel with the external flow validation effort, a level-set based embedded boundary method was tested in CLSVOF using a hollow cylinder to mimic a simple injector. In the embedded approach, computational cells in a narrow band inside the wall are used to mimic no-slip boundary conditions for an arbitrary wall surface, which is captured as a level set. In collaboration with Florida State University, we found that different discretization techniques (upwind vs. semi-Lagrangian) of the nonlinear advective force terms in the Navier-Stokes equation can introduce more or less disturbance on the surface of the ejected liquid. This aspect is currently being evaluated in grid convergence studies.

Significance:
The project is aimed at providing a better understanding of high-pressure internal flow effects on spray formation. Existing engineering models lump such effects in constants that need to be calibrated with preexisting measurements. However, increased predictive capability of fuel/air distribution in engines over the full range of operation conditions is demanded by the trend of increasing fuel injection pressure in the automotive industry. This project is focused on the subcritical state of the injected fuel and is, therefore, complementary to the ongoing development at the Combustion Research Facility (CRF) of a large eddy simulation capability in the supercritical regime. This activity is also coordinated with the Engine Combustion Network (ECN) initiative, for instance in the choice of the simulation conditions and of the nozzle geometry for diesel injection. The ECN group is currently investigating the effect of the sensitivity of spray characteristics to injector geometrical imperfections due to the manufacturing process. These effects will be captured by the embedded wall method that has been added to the code. Overall, the physics-based, high-fidelity simulations enabled by this project are expected to provide new insight of the fuel injection mechanism and help broaden the predictive capability of existing computational fluid dynamics models.

Beyond engine applications, the implementation of realistic two-phase equations of state and the introduction of compressibility effects in a code that can track multiple sharp interfaces in problems scaling up to several hundred processors will be an almost unique asset for Sandia. It will enable, for instance, the study of complex fluids behavior in a disruptive environment (caused by a blast, for instance, in a national security scenario), or the study of the internal flow characteristics of two-phase heat transfer devices.

Multilevel Summation Methods for Efficient Evaluation of Long-Range Pairwise Interactions in Atomistic and Coarse-Grained Molecular Simulation
157688

Year 1 of 3
Principal Investigator: S. D. Bond

Project Purpose:
The availability of efficient algorithms for long-range pairwise interactions is central to the success of numerous applications, ranging in scale from atomic-level modeling of materials to astrophysics. Molecular dynamics (MD), in particular, can require months of supercomputer time, due to the expense of the large number of force evaluations required. The challenge is to design reliable, efficient, portable, scalable algorithms for calculating long-range interactions in large systems. Scalability and portability are of particular concern for modern exascale supercomputers with hybrid architectures and massive numbers of processors. A diverse set of methods has evolved for rapid approximation of long-range interactions, including fast-multipole methods and Fourier-based particle-mesh Ewald methods. Multipole methods excel when applied to systems with large variations in density (e.g., astrophysics), but have generally been considered less competitive for more uniform systems (e.g., molecular dynamics). As a result, state-of-the-art MD codes like NAMD and LAMMPS, use particle-mesh Ewald.

Due to the use of the Fast Fourier Transform (FFT), particle-mesh Ewald methods do not scale well as the system size is increased, with a computational cost proportional to N log N, where N is the number of atoms. The FFT also has a large communication overhead, due to the parallel scalability problems associated with the matrix transpose. This project will focus on the development and analysis of the multilevel summation method (MSM), which is a relatively new algorithm for computing pairwise interactions. Compared to particle-mesh Ewald methods, the MSM is lesser known, with the first MD studies appearing within the last five years. Preliminary studies have found that it has a computation cost proportional to N, rather than N log N, and relatively low communication overhead (uses nested grids instead of the FFT). Development of this method has the potential to dramatically improve the efficiency of MD software used for predictive simulation of materials.

Summary of Accomplishments:
We wrote prototype code to assist with the development of algorithms for computing long-range pairwise interactions. The initial code has been implemented in MatLab to allow for rapid testing, and comparison with other competing algorithms. We tested the prototype code on a set of test problems in various dimensions. Preliminary results are encouraging.

Significance:
The development of more efficient algorithms for the evaluation of long-range pairwise interactions will enable molecular dynamics simulation of larger systems with more accurate material models. If successful, this research will significantly improve the scalability of simulation software, allowing for more efficient use of the massive numbers of processors in modern supercomputers. Ultimately, enabling larger simulations will enhance the predictive capability of software used for modeling materials of interest to the DOE.

Predicting the Future Trajectory of Arctic Sea Ice: Reducing Uncertainty in High-Resolution Sea Ice Models
157957

Year 1 of 3
Principal Investigator: K. J. Peterson

Project Purpose:
The purpose of this project is to improve fidelity of sea ice models and to develop methods to compare and propagate their uncertainties in order to provide new predictive capabilities for use in decision support.

Current generation Earth System Models (ESMs) vary greatly in their predictions for Arctic sea ice evolution, but all have underestimated the rate of decline in minimum sea ice extent over the last thirty years. Sea ice components of ESMs are multiphysics models with complex choices in the physical submodels and parameterizations used to define the governing equations and in the numerical methods used to discretize and solve the governing equations. They also contain many physical parameters with values that are inherently uncertain. A robust, predictive sea ice modeling capability requires an understanding of how uncertainties are propagated by different numerical algorithms and a consistent approach for comparative evaluation of the physical fidelity of each model.

A novel framework for calibrating and validating sea ice models using satellite and submarine data from the Arctic is being used. The objective is to develop a systematic methodology to: 1) evaluate predictive capabilities of sea ice models, 2) discover the most important physical parameters contributing to uncertainties, and 3) assess the impact of numerical algorithms on sea ice simulations. Several sea ice models and model configurations will be used to develop and test our approach. Alternative numerical implementations and physical models will be evaluated using the validation framework in order to determine the most relevant improvements. A distinguishing characteristic of the research is coordination of efforts in uncertainty/sensitivity analysis, physical modeling, and advances in numerical algorithms.

Summary of Accomplishments:
The work in FY 2011 has focused on code improvements necessary for the sensitivity analysis and model optimization. These improvements will enhance the capabilities of the two sea ice models under consideration (Los Alamos National Laboratory [LANL] CICE and MPM) and provide a level basis of comparison. Under this task a new branch of CICE that includes the elastic-decohesive (E-D) constitutive model has been created in coordination with LANL, and a preliminary implementation of the E-D model has been completed. Research into the appropriate lateral melting and ocean mixed model algorithms for MPM has been completed and a new branch of MPM has been created combining previous code improvements from Sandia and the University of New Mexico. A simple box domain simulation has been set up in both CICE and MPM for testing purposes. Background research into numerical techniques for the code optimization and validation framework has begun.

Significance:
Climate change is a significant national security threat and the loss of Arctic sea ice is one of its most obvious manifestations. This project will eventually provide a modeling capability that more accurately reproduces the Arctic sea ice distribution of the past decades and, more importantly, better predicts the future rate of sea ice loss.

Implementation of the elastic-decohesive rheology in the LANL CICE model will benefit collaborators at LANL by providing an alternative rheology that will more realistically approximate sea ice deformation on smaller scales. Additionally, once testing is complete, this new capability can be delivered to the wider sea ice and climate modeling community through the Community Earth System Model (CESM), which contains a variant of CICE as the sea ice component. Improvements in the MPM sea ice model will benefit collaborators at the Jet Propulsion Laboratory and the University of New Mexico, who are working to couple the model with the Massachusetts Institute of Technology general circulation model (MITgcm). In turn, the coupled system of models can be used in some phases of the optimization work in this project to test the performance of a coupled ice-ocean model in comparison with a standalone sea ice model. Research into effective techniques for optimization, validation, and uncertainty quantification will lead to a new framework for calibrating and validating multiphysics, multifidelity models.

High-Performance Graphics Processor-Based Computed Tomography Reconstruction Algorithms for Nuclear and Other Large Scale Applications
158182

Year 1 of 3
Principal Investigator: E. S. Jiménez Jr.

Project Purpose:
The goal of this work is to develop a fast computed tomography (CT) reconstruction algorithm based on graphics processing units (GPU) that achieves significant improvement over traditional central processing unit (CPU)-based implementations. The main challenge in developing a CT algorithm that is capable of handling very large datasets is parallelizing the algorithm in such a way that data transfer does not hinder performance of the reconstruction algorithm.

General Purpose Graphics Processing (GPGPU) is a new technology that the S&T community is starting to adopt in many fields where CPU-based computing is the norm. GPGPU programming requires a new approach to algorithm development that utilizes massively multithreaded environments. Multithreaded algorithms in general are difficult to optimize since performance bottlenecks occur that are nonexistent in single-threaded algorithms such as memory latencies. If an efficient GPU-based CT reconstruction algorithm can be developed, computational times could be improved by a factor of 20. Additionally, cost benefits will be realized as commodity graphics hardware could potentially replace expensive supercomputers and high-end workstations.

Development of a fully optimized reconstruction algorithm may require a dramatic restructuring of the entire algorithm in order to achieve optimal performance. This project will take advantage of the Compute Unified Device Architecture (CUDA) programming environment and attempt to parallelize the task in such a way that multiple slices of the reconstruction volume are computed simultaneously. This work will also take advantage of the GPU memory by utilizing asynchronous memory transfers, GPU texture memory, and (when possible) pinned host memory so that the memory transfer bottleneck inherent to GPGPU is amortized. Additionally, this work will take advantage of GPU-specific hardware (i.e., fast texture memory, pixel-pipelines, hardware interpolators, and varying memory hierarchy) that will allow for additional performance improvements.

Summary of Accomplishments:
We have discovered various hardware components specific to graphics processors (GPU) that can be utilized to realize improved performance over the 5-6 x computational speedup of GPUs versus central processing units (CPU). We have designed and developed a working version of our algorithm for a single GPU. This single GPU version was tested using a dataset that is representative of a typical industrial dataset (800 x 800 pixel slices, 720 projections), a large industrial dataset (10,000 x 10,000 pixel slices, 10,000 projections), and an academic dataset (~1 billion pixel slices, 16,000 projections). We have demonstrated that a GPU-based algorithm is approximately 193 times faster than a single-threaded CPU reconstruction method and 25 times faster than a multithreaded algorithm using 24 computational threads for typical industrial datasets. A speedup of 258x was realized using GPU methods versus a single threaded algorithm and 23x for the multithreaded method for large datasets. The academic dataset showed a speedup of 260x using GPU methods versus single-threaded methods and a 20x speedup when GPU methods are compared to a multithreaded method.

We have learned that data transfer and file traffic is only a bottleneck for typical datasets and is less of a problem for larger sized datasets using a single GPU. Using solid-state disks seems to alleviate the file reading and writing bottlenecks. Memory transfer between CPU-based memory and GPU-memory is not significant with current implementation for the single GPU algorithm. This will be reassessed once a multi-GPU algorithm is developed.

Significance:

A computed tomography reconstruction algorithm based on GPUs allows for faster and cheaper reconstruction using commodity graphics hardware instead of expensive supercomputers. Additionally, the task will be completed in less time for most cases. All of Sandia's national security missions will benefit from technologically advanced reconstruction solutions. Nuclear weapons, nonproliferation, energy and infrastructure, and defense systems use CT to inspect, diagnose and validate parts and structures for quality. Homeland security uses CT at ports of entry to inspect incoming vehicles and cargo for contraband. Sandia's reputation in ST&E will be strengthened by contributing to a new technology that is dramatically changing supercomputing architectures.

Sandia has already benefitted from this work. This algorithm in its single-GPU form is already being used for various projects as an alternative for comparative results in CT-reconstruction and nondestructive testing. Lab capabilities will certainly be expanded in testing, modeling, evaluation, and fabrication. This work can help streamline and speed up work within Sandia and allow the Laboratories to efficiently and effectively obtain fast results on various projects.

Sublinear Algorithms for Massive Data Sets
158477

Year 1 of 3
Principal Investigator: S. Comandur

Project Purpose:
Our ability to accumulate and store data is increasing rapidly. More and more, we are faced with massive data sets. These could be Internet graphs, network traffic data, or genetic sequences of various organisms. Having gathered this data, we face the problem of processing it to learn something meaningful. In many cases, the data is too vast to complete even a single read pass through it. We need to be able to perform a sublinear analysis (i.e., an analysis that looks at a tiny fraction of the data). The goal is to determine nontrivial properties of the data, such as recurring patterns in a string, sparse cuts in graphs, or communities in a cyber network.

The statistical approach to large data is to choose an appropriate random sample, and extrapolate from the sample. But different combinatorial or graph problems may require different kinds of samples. The main challenge is to develop special problem-specific sampling techniques. This is the heart of sublinear analysis.

Over the past decade, the theoretical computer science and discrete mathematics community have developed many algorithmic sampling tools for sublinear algorithms. This has been an exciting area of theoretical study, but there has been almost no work on bringing this to the practical regime. Our aim is to bridge this gap and apply these theoretical techniques to the various massive dataset problems at Sandia. It would be worthwhile to see how these tools can be applied to real-world massive graphs.

The theory of sublinear algorithms has yielded a small class of basic sampling procedures that are believed to be applicable for a large variety of problems. One of the major aims of this work is to verify this, and develop more effective variants of these methods. The various practical problems will also lead to new theoretical questions of interest.

Summary of Accomplishments:
One of the initial goals of this project is to determine possible areas of applications of sublinear algorithms. We had discussions about using sublinear graph algorithms for dealing with massive streaming graphs. We plan to develop algorithms based on these techniques.

A major concern regarding the streaming graphs project is discovering good synthetic inputs and test cases. For testing new sublinear algorithms, we need to find good ways of generating massive data. We are working on new scalable models for efficient graphs. We designed and analyzed a new model which seems very promising in its ability to reflect real graphs. We discovered that sublinear sampling methods might have applications in processing the massive data that combustion simulations (done by the Combustion Research Facility) generate. Collaborators are working on algorithmic frameworks for dealing with the large data that these simulations output. We feel that sublinear techniques can be used to greatly speed up some of their computations. They already use some sampling approximations, and we are beginning to work on understanding and enhancing these.

In theoretical work with Rutgers University, we developed a new streaming algorithm for detecting increasing sequences. This is based on new sublinear techniques that we had developed. The results are being written as a research paper.

Significance:
Our methods enable faster analysis of massive data, and we focus on large arrays and graphs. Large arrays appear in many cyber security applications (e.g., network traffic data, or samples of malware). An important aspect of studying these is to find recurring patterns or common portions between various arrays. We target these applications in this work. Large graphs are often used to represent communication between various entities (network of computers, cellular phones, etc.). Detecting anomalies or patterns in these networks would require algorithms that can scale to large data sets. This can have a major impact on cyber security applications.

A concrete application that appears promising is the use of sublinear algorithms to deal with massive data generated by combustion simulations. We are currently developing this line of research. Sampling mechanisms also have use in the analysis of massive graphs. In recent work, we required some sampling techniques to speed up graph diagnostic algorithms. The understanding and analysis of these techniques come directly from methods for sampling random variables. Without these tools, we would not have been able to run our diagnostics of real graphs because of scalability issues.

Accurate Model Development for Large Eddy Simulation of Turbulent Compressible Flow Problems
158482

Year 1 of 3
Principal Investigator: M. Howard

Project Purpose:
Accurate simulation of turbulence is vital for predicting complex physical flow behaviors. Turbulence spans a large range of time and length scales and capturing all of its effects is difficult. Direct numerical simulation is too computationally intensive for high Reynolds number problems. Reynolds averaged Navier-Stokes simulations are less accurate and often inapplicable to many problems. Large eddy simulation (LES) resolves the predominant flow features and models the smaller scale turbulence. Of these approaches, it is clear that LES offers the best promise, but several significant challenges exist for compressible problems. Appropriate subgrid scale modeling is an open area of research, especially for supersonic flows. Higher-order accurate numerical methods are essential to reducing discretization error. The interaction of the subgrid scale model and the discretization method is also an important factor that is not fully understood. The investigation of these areas requires an efficient and scalable algorithm and poses significant challenges for accurately predicting complex turbulent compressible flows.

This research effort is motivated by the assertion that a systematic investigation of unstructured discretization methods, filtering and subgrid scale modeling techniques and the interactions between them, combined with a focus on accuracy and scalability, will enable an LES capability that surpasses existing limitations for solving turbulent compressible flow problems of national interest. We will rigorously identify the defining theoretical and numerical features of a successful LES scheme, and then develop a state-of-the-art capability for accurate unstructured LES of compressible flows. Two spatial discretization methods as well as implicit, explicit, and hybrid time integration techniques will be explored. This will enable us to make broad assessments about discretization characteristics that few existing research efforts have addressed. Determining the merits of each discretization feeds directly into investigating appropriate filtering techniques, subgrid scale models, discretization errors and their interplay for this class of flows, all poorly understood topics.

Summary of Accomplishments:
We designed and developed a baseline detached eddy simulation (DES)/LES capability within a mixed discretization research computational fluid dynamics (CFD) code. This code is the basis for the exploratory computational work that will be done throughout the duration of this project. One of the defining features of the research code is the ability to support multiple discretizations, that is both finite element and finite volume schemes, in order to investigate the performance of both. Within a finite volume context, the ability to use hybrid structured and unstructured discretizations is a key aspect for demonstrating higher-order accuracy with the benefits of unstructured grid flexibility.

To date, two external collaborations have been established that will positively affect the direction of this work. Interactions with Professor Graham Candler and his research group at the University of Minnesota have and will continue to leverage this considerable experience with finite volume methods for high-speed turbulent reacting flows. Professor Ken Jansen and his research group at the University of Colorado will serve as a consultant and collaborator for DES/LES of turbulent flows in a finite element context.

Significance:

The ability to accurately predict high-speed turbulent compressible flows greatly impacts national nuclear security missions. This work finds application to gravity bomb (DOE/NNSA, DoD) and hypersonic re-entry and cruise vehicle (DOE/NNSA, DoD, NASA) design and qualification. The current state-of-the-art in predictive capabilities for problems in these flow regimes does not produce high enough fidelity to accurately capture the physics for qualification purposes. This research effort aims to develop a capability that will establish Sandia as a leader in computational methods for accurate prediction of turbulent compressible flow phenomena and will directly impact ongoing and future stockpile Life Extension Programs.

Heterogeneous Scalable Framework for Multiphase Flows
158997

Year 1 of 3
Principal Investigator: K. V. Morris

Project Purpose:
Computational modeling of turbulent combustion is vital for our energy infrastructure and offers the means to develop, test, and optimize fuels and engine configurations. In the case of internal combustion engines, fuel injection simulations provide insight into the required calibration for appropriate turbulent mixing and efficient combustion. In modeling the dilute spray regime, away from the injection site and downstream of the atomization processes, considerable doubts persist regarding how to best parameterize and predict the various two-way couplings between the dispersed phase and the surrounding fluid turbulence. These couplings include mass, momentum, and energy exchanges.

Two categories of challenges confront the developer of computational spray models: those related to the computation and those related to the physics. Regarding the computation, the trend towards heterogeneous, multi- and many-core platforms will require considerable re-engineering of codes written for a specific supercomputing platform. Regarding the physics, accurate methods for transferring mass, momentum and energy from the dispersed phase onto the carrier fluid grid have so far eluded modelers. Significant challenges also lie at the intersection between these two categories. To be competitive, any physics model must be expressible in a parallel algorithm that performs well on multiple computer platforms. To exploit the countless computing hardware configurations available, and confront the challenges regarding portability and performance optimization for current scientific applications, this project will develop a novel software architecture that segregates the data computation and communication from the physical models. This architecture will increase the versatility of present and future scientific codes. Current state-of-the-art spray model computations predict experimental results only for a narrow band of particle length and time scales. This work will simultaneously address a fundamental need to generalize these models to account for a wider range of particle scales.

Summary of Accomplishments:
Initial work in the first abbreviated project year has concentrated on modifying the scripts that were previously used to automate the creation of the bindings necessary to support Object-Oriented Fortran 2003 interfaces to Trilinos packages. The modified scripts should prove more flexible for incorporating changes that will allow wrapping templated C++ packages, Tpetra, and Kokkos. These packages are required to provide a platform independent parallel environment. In order to take advantage of the dual nature of the project, we have developed candidate object-oriented designs based on abstractions that leverage existing Trilinos constructs.

Significance:
The DOE Office of Energy Efficiency and Renewable Energy has identified the improving of the predictive simulation of internal combustion engines as a key component of our nation’s energy security. Our interactions with engine manufacturers suggest that providing a better understanding of spray dynamics, even in the nonreacting flow regime, will significantly improve the manufacturers’ simulation capabilities. Our interactions with computational fluid dynamics software vendors indicate that current commercial codes have difficulty scaling beyond a few dozen cores. This project addresses critical needs of both communities and ties to the DOE Office of Energy Efficiency and Renewable Energy.

Interaction-Driven Learning Approaches to Complex Systems Modeling
159005

Year 1 of 3
Principal Investigator: A. V. Outkin

Project Purpose:
Combining interaction-driven and machine learning models into one cohesive framework will allow Sandia to develop complex systems models that will collect, interpret, and adapt in real time the model parameters and structure while harnessing the predictive power inherent to interaction-driven models. While interaction-driven models provide significant predictive and explanatory power, they often require lengthy validation and calibration and generally cannot be used for real time decision-making. Additionally, once great effort is expended to carefully calibrate and validate these models, the real-world structure that the model was built to represent may have already changed or evolved, making the model obsolete.

Machine learning can process large datasets and learn complex rules from observable system inputs. However, machine learning does not provide a fundamental understanding of how results were generated or when they became invalid; nor does it provide predictions regarding interventions. This is where the interaction-driven models will constrain the adaptation of learning models to the fundamental "truths" that lie within the system. We will prove and cross-validate this approach on information-rich domains such as opinion dynamics. Developing this framework will enable analysts to use partially calibrated interaction-driven models for prediction in real-time. It will reduce demands on model validation and allow the modelers to focus on the logic driving the system and generating its dynamics. It will place Sandia in leading role to provide decision support when information is incomplete and quick or real-time actions are necessary, including response to natural or man-made disasters, sensor data processing, and cyber security.

Summary of Accomplishments:
During the truncated first year phase of this project, we have completed the following tasks:
- Developed an initial conceptual model that combines the interaction-driven models and sensor networks observations into a cohesive learning model.
- Conducted a literature review and identified related approaches in the sensor networks literature.
- Implemented an initial prototype framework for connecting interaction-driven models to a learning framework and tested it using an existing model of a network.
- Developed a preliminary demonstration showing that randomly generated interaction models with correct causal structure may have predictive power.
- Created a prototype learning framework estimation and visualization scripts in R.
- Started developing external collaborations.

Significance:
Successful completion of this project will improve DOE's capability to model and manage complex systems in real time based on incomplete data and on partially calibrated interaction-driven models. Complex systems, such as global energy systems, are of fundamental importance to the goals and missions of the DOE. Success of this approach will greatly improve the predictive and explanatory power of new or existing models developed for national security missions including understanding terrorism, sensor data gathering and processing, military planning, panic behavior, and societal influence.

Transactions for Resilience and Consistency in Integrated Application Workflows for High Performance Computing
159006

Year 1 of 3
Principal Investigator: G. F. Lofstead

Project Purpose:
The scientific discovery process often involves a series of steps that may include simulation, analysis, and visualization with intermediate results staged on the storage system. For large-scale applications, the time, space, and power overhead of storing transient data is already overwhelming and will increase as machines and applications continue to increase in scale. Given these challenges, there is tremendous benefit in coupling these steps as an "integrated application workflow" (IAW). This approach eliminates storing transient data on the storage system but introduces new challenges with respect to resilience and data consistency.

For Sandia's CTH (CSQ to the three halves) shock physics code, understanding dynamics of material fragments, fragment tracking, is key for scientific insights. Generating fragment information requires separate analysis on the raw CTH data at every time step. An IAW for fragment detection eliminates the need to persistently store intermediate results making tracking fragments practical. Resilience is imperative because a failure or data corruption anywhere in the IAW invalidates the result. Dramatic changes in data management must be made to achieve exascale computations. IAWs represent a fundamental change in the way computational science leads to insight; however, without resilience, IAWs are not practical at scale. A transaction-based technique provides a robust and scalable solution to resilience for IAWs

Traditional distribution transaction management systems focus on a single client with multiple servers (1-N). For the high performance computing (HPC) environment, however, there are potentially millions of clients interacting with thousands of servers (M-N). Collective input-output (IO) is an existing M-N style operation for HPC. To reduce the number of small IO operations, an initial phase rearranges data across the M processes before writing to N storage targets. The extreme overhead at scale shows what not to do while giving hints on how to manage some of the tasks, such as identifying the group of processes as a whole and the total amount and distribution of data.

Summary of Accomplishments:
In the approximately two months since this project's inception, we have demonstrated a simplistic implementation of the transaction protocol through the work of a summer student. This work has been demonstrated to function at small scale, but the itemized scaling tests and mitigation measures still need to be considered to ensure that decisions made for the initial implementation will prove scalable.

Significance:
There is increasing national interest in exascale computing, as demonstrated by the recent announcement of $126 million for exascale computing set aside in President Obama's budget proposal. Our project specifically addresses one of the largest challenges for exascale computing, efficient data management, and has the potential to considerably impact the way large-scale codes integrate simulation, analysis, and visualization. This technology is directly relevant to the large-scale applications developed for the advanced simulation and computing program, and it is also applicable to a number of other applications in the open science community including fusion, climate, and even cyber security.

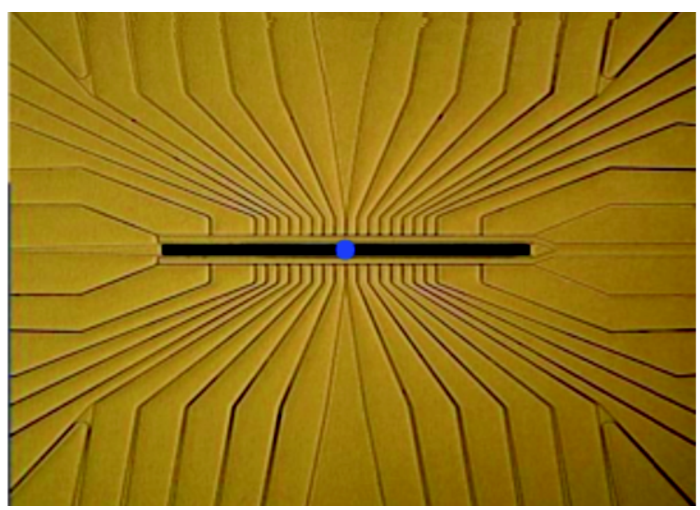
NANOSCIENCE TO MICROSYSTEMS INVESTMENT AREA

This investment area (IA) funds both fundamental and applied research into phenomena that arise from the distinctive properties of matter at the nanoscale (billionths of a meter), the scale of single atoms, small clusters of atoms, and small molecules, and of structures at the microscale (millionths of a meter). This includes both inorganic nanoparticle research and applications, for example, single atomic nanoparticles of metals such a gold, and also biological nanoparticles and nanomachines — and often, the combination of inorganic and biological, with bio-nanostructures sometimes providing models for developers to emulate.

Applications range from micromachines such as tiny heat engines and microelectromechanical systems (MEMs), to quantum cascade lasers to improved computer memories and new types of computing data structures (as in quantum computing), as well as nano- and microstructures showing novel optical and electromagnetic properties that tend not to be observed at larger scales. In addition to fundamental insights into the nature of materials and nanostructures, this IA ultimately offers solutions to problems in energy security, climate change, secure communications, cryptography, remote sensing and threat detection, and other arenas germane to national and global security.

Ion-Photon Quantum Interface: Entanglement Engineering
Project 148549

This project studies the entanglement of photons with trapped ions, as another step forward in the design of the fundamental elements — quantum bits (qubits) — for quantum computation. Trapped ion qubits are favored for their long coherence times (the interval during which their quantum state reliably stores information before decoherence occurs). However, in order to transmit this information among the elements comprising a quantum computer, photonic qubits are the natural choice because they can quickly travel long distances with a minimum of information loss (decoherence). Cavity quantum electrodynamics (QED) studies the high-efficiency of single-photon collection from a trapped ion, with the ion-trap altering the electromagnetic environment of a trapped single particle, such that photon emission is enhanced. This project has designed and fabricated a radio-frequency-optimized ion trap for ion-photon cavity quantum electrodynamics (cQED) experiments, and has also completed the theoretical design and experimental testing of the cavity mirrors for the quantum electrodynamics (QED) apparatus, permitting the imaging of an ion from the trap surface so as to increase fluorescence light collection.



Sandia-designed Ion Trap

Bio-Inspired Nanocomposite Assemblies as Smart Skin Components
Project 130769

This project is biomimetic, given that it seeks, through the use of a host matrix of lipid bilayers (the fundamental structural motif of living cell membranes) to create smart membranes by inserting functionalized nanoparticles into this host lipid matrix. This represents an attempt to mimic the electrochemically responsive ion channels in biological membranes, proteins that open and close in response to either changes in transmembrane voltage or chemical signals. Such an achievement could then potentially produce smart-skin materials for responsive, self-regulating sensors either for detection of threats or as materials for adaptive military camouflage. The project has succeeded in depositing gold nanoparticles (NPs) into the lipid bilayer membrane, and by varying the surface charge density of both NPs and supporting lipid bilayers, either deposit the NPs at the membrane surfaces or disrupt the membranes, the consequence of these interactions monitored by atomic force microscopy and fluorescence microscopy. By varying the chemistry, an initially uniform distribution of gold NPs was induced to form gold nanorings. Theoretically, the project applied a new fluids density functional theory, the modified-inhomogeneous statistical associating fluid theory (iSAFT), to calculations of the structure and thermodynamic properties of coarse-grained models of lipid bilayers that are consistent with experimental results.

Formation of gold nanoring (right) from a more uniform distribution of gold nanoparticles (left) within a lipid bilayer.

Nanoscience to Microsystems Investment Area

Architecturally Controlled Nanocathode Materials for Improved Rechargeable Batteries
130767

Year 3 of 3
Principal Investigator: E. D. Spoerke

Project Purpose:
Rechargeable batteries are key to the continued advance of electric or hybrid electric vehicles, clean energy harvest of renewable power, improvements in utility grid efficiency, and energizing energy-hungry portable electronics. Large-scale systems (transportation and utilities) especially require safe, cost-effective batteries with stable, high energy densities — demands current battery technologies are unable to satisfy. We aim to address this issue by developing an improved cathode with an emphasis on creating "high capacity" electroactive materials. Although it is possible to increase energy density in these systems by increasing either voltage or capacity, our capacity-based approach avoids a host of serious, often dangerous, side-effects including electrolyte degradation, current collector corrosion, binder deterioration, and other deleterious side reactions commonly associated with higher voltage cathodes. Increasing capacities in these systems requires controlling the phase transitions that occur during electrochemical cycling of the cathode. We aim to create the three-phase equilibria responsible for voltage plateaus in a cathode discharge cycle. These voltage plateaus represent dramatic extensions of capacity at elevated voltages, but because these plateaus have traditionally occurred at low voltages in iron oxides, these materials have been largely ignored. Our challenge is to find the phase equilibria in the iron oxide system that produces stable, cyclable plateaus at cathodic voltages at room temperature.

Our unique approach uses low-cost iron oxides to create moderate voltage, high-capacity cathode materials capable of high energy densities, while offering significant safety and reliability advantages over high-voltage alternatives. Achieving these goals requires an integrated, understanding-based approach to materials development. Our team assimilates computational modeling, designer chemical syntheses, and state-of-the-art materials and electrochemical characterization to understand the relationships between electrochemical performance and materials structure and chemistry. In addition, our synthetic capabilities provide us with the means to synthesize the diverse target phases necessary to explore the Li-Fe-O phase space.

Summary of Accomplishments:
We have synthesized, characterized, tested, and modeled the electrochemical activity of a wide range of iron oxide-based materials as cathodes in lithium ion battery systems. In the course of this work, we have come to identify select iron oxide phases with specific materials traits and properties that make them attractive candidates both as low-moderate voltage cathodes (for applications such as stationary power) or as low-cost, safety-conscious alternatives to carbon anodes. In identifying these compounds, we have also developed expertise with respect to the balance of materials, not suitable for electrochemical applications, gaining a detailed understanding of the fundamental materials properties that distinguish the different candidate oxides. In addition to identifying target materials themselves, we have also evaluated the influence of material morphology and size on the electrochemical performance of these materials, and we have concluded that among the materials studied here, material phase plays a much greater role in electrochemical performance than either particle size or shape. Finally, our studies probed the effects of elemental doping of select iron oxide phases, and we were able to identify a general set of criteria that may be used to direct the doping of not only iron oxides, but other materials as

well in trying to improve the electrochemical performance and stability electrode materials in lithium ion battery systems. Perhaps just as important as the results specifically related to electrical energy storage, our team has also developed extensive synthetic expertise that has already proven valuable to additional existing and new projects interested in studying custom iron oxide materials.

Significance:

This energy-related project on battery materials research seeks to develop new science and technology related to energy storage, an important national and global topic, and a priority of the DOE. Project success will provide valuable new insight into battery materials research with potentially significant impact on energy storage for transportation, capturing renewable energy, improving power grid efficiency, and powering both consumer and military portable electronics.

Refereed Communications:

T.J. Boyle, L.A.M. Ottley, C.A. Apblett, et al., "Synthesis, Characterization, and Electrochemical Properties of a Series of Sterically Varied Iron(II) Alkoxide Precursors and their Resultant Nanoparticles," *Inorganic Chemistry*, vol. 50, pp. 6174-6182, July 2011.

Bio-Inspired Nanocomposite Assemblies as Smart Skin Components
130769

Year 3 of 3
Principal Investigator: S. M. Brozik

Project Purpose:
There is national interest in the development of sophisticated materials that can automatically detect and respond to chemical and biological threats without the need for human intervention. In living systems, cell membranes perform such functions on a routine basis, detecting threats, communicating with the cell, and triggering automatic responses such as the opening and closing of ion channels. The purpose of this project was to learn how to replicate simple threat detection and response functions within artificial membrane systems. The original goals aimed at developing “smart skin” assemblies included, 1) synthesizing functionalized nanoparticles to produce electrochemically responsive systems within a lipid bilayer host matrices, 2) calculating the energetics of nanoparticle-lipid interactions and pore formation, and 3) determining the mechanism of insertion of nanoparticles in lipid bilayers via imaging and electrochemistry.

There are a few reports of the use of programmable materials to open and close pores in rigid hosts such as mesoporous materials using either heat or light activation. However, none of these materials can regulate themselves in response to the detection of threats. The strategies we investigated in this project involve learning how to use programmable nanomaterials to automatically eliminate open channels within a lipid bilayer host when “threats” are detected. We generated and characterized functionalized nanoparticles that can be used to create synthetic pores through the membrane and investigated methods of eliminating the pores either through electrochemistry, change in pH, etc. We also focused on characterizing the behavior of functionalized gold nanoparticles (NPs) in different lipid membranes and lipid vesicles and coupled these results to modeling efforts designed to gain an understanding of the interaction of nanoparticles within lipid assemblies.

Summary of Accomplishments:
Theoretically, we applied a new fluids density functional theory, the modified-inhomogeneous statistical associating fluid theory (iSAFT), to calculations of the structure and thermodynamic properties of coarse-grained models of lipid bilayers. We have detailed methods for systematic coarse-graining of lipid molecules using experimental measures to guide the optimization of the models. The approach involves utilization of a diverse set of numerical techniques within the density functional theory (DFT), including high-performance solvers, bifurcation algorithms, and inhomogeneous boundaries. This approach results in coarse-grained lipid bilayer models in which the properties of the underlying constituent groups are consistent with those of real materials. Additionally, the models result in lipid bilayers with structural and elastic properties that are consistent with experimental measures.

Experimentally, we have varied the surface charge density of both NPs and supporting lipid bilayers, and monitored the consequence of their interactions by atomic force microscopy and fluorescence microscopy. Depending on their surface charge densities, negatively charged AuNPs can deposit at the membrane surfaces or extract the oppositely charged dioleoyltrimethylammonium propane (DOTAP) molecules to disrupt the membranes. The membrane disruption selectively occurred in the fluidic domains. The particle deposition was uniform over the surfaces of DOTAP and DOTAP- 2-oleoyl-1-pamlitoyl-*sn*-glyecro-3-phosphocholine (POPC) bilayers, an indication of homogeneous charge distribution; while at nanostructured DOTAP-distearoyl phosphatidylcholine (DSPC) surfaces, the AuNPs were deposited into the network structures. This work demonstrated that the surface charge localization could lead to localized membrane disruption and particle deposition. We have also demonstrated that a combination of the unique properties of DOTAP lipid bilayer assemblies (LBAs) and zirconium coordination chemistry of partially carboxylated AuNPs resulted in the formation of gold nanoring nanostructures. These structures rely on the native lateral fluidity of the LBAs, the pH response of the LBAs to the $ZrCl_4$ and zirconium coordination of the AuNPs.

Significance:
In this work we were able to synthesize functionalized nanoparticles to produce electrochemically responsive systems; calculate the energetics of NP/lipid interactions and pore formation; and, determine the mechanism of insertion of NPs in lipid bilayers via imaging and electrochemistry. The military, DHS, and Defense Threat Reduction Agency (DTRA) are each interested in the development of responsive films or fabrics to meet two mission needs: 1) responsive materials for protecting personnel from chemical and biological threats, and 2) materials for adaptive camouflage. The work conducted will provide the scientific underpinnings for achieving both of these goals by mimicking the responsive behaviors that occur in cellular membranes. For Sandia's science missions, the development of biomimetic nanocomposites is one of the frontier areas in nanoscience that maps onto the joint Sandia/Los Alamos Basic Energy Sciences (BES)-funded Center for Integrated Nanotechnologies (CINT).

Refereed Communications:
X. Xiao, G.A. Montaño, A. Allen, K.E. Achyuthan, D.R. Wheeler, and S.M. Brozik, "Lipid Bilayer Templated Gold Nanoparticles Nanoring Formation Using Zirconium Ion Coordination Chemistry," *Langmuir*, vol. 27, pp. 9484-9489, June 2011.

Enabling Graphene Nanoelectronics
130771

Year 3 of 3
Principal Investigator: S. W. Howell

Project Purpose:
The isolation of graphene monolayers in 2004 has spurred an explosion of international graphene research interest due to its exotic Dirac Quantum Mechanics-based electronic properties. Although intrinsically a high-mobility semi-metal (~200,000 cm^2/Vs when defect-free, versus ~1500 for Si and ~8500 for GaAs), graphene's physical strength, adaptability to planar processing, micron-scale room temperature ballistic electronic transport behavior, and potential for band gap engineering manipulation (via chemical doping or application of internal/external electric fields) make it a promising candidate for advancing and possibly replacing silicon technology in the nanoscale regime, as well as the creation of disruptive high-speed carbon electronic architectures. The promise of graphene, as a high-performance electronic material, has recently attracted the interest of Defense Advanced Research Projects Agency, as well as DOE's Basic Energy Science. Currently, a large amount of research has concentrated on materials and single devices made from randomly placed small graphene domains (often from manually exfoliated highly oriented pyrolytic graphite (HOPG). To realize graphene's electronic device potential, techniques must be developed to reproducibly deposit/synthesize high quality graphene onto technologically relevant surfaces over large areas, which is difficult due to a lack of fundamental understanding of graphene formation and related defects.

To address this major scientific and technological bottleneck in graphene device development, we will develop differentiating and synergistic approaches that include the following: 1) development of routes for graphene synthesis on SiC and metal (such as copper) substrates, including necessary understanding of nucleation/growth to achieve large area (100 μm^2) domains; 2) methods for transfer on relevant surfaces; and 3) improving the understanding of intrinsic graphene and relevant defects for nanoelectronics (including the observation of mobilities beyond the presently observed defect-limited ~10,000 cm^2/Vs towards the suggested ~200,000 cm^2/Vs limit from exfoliated samples). The linkage to a complete suite of coordinated Sandia characterization/modeling efforts is another differentiating factor of our project that ensures project impact and leadership within the competitive and rapidly moving graphene research community.

Summary of Accomplishments:
During the last year of this project, we made the following key accomplishments:

1. Developed graphene synthesis using atmospheric Ar and high temp
   - Achieved domain size of 100 μm^2
   - Observed record electron mobility (14000 cm^2/Vs)
   - Achieved excellent uniformity across sample
   - Developed understanding of mechanisms for graphene growth on SiC
   - Developed strategy for bilayer graphene wafer scale growth
2. Developed graphene growth by depositing carbon on SiC
3. Developed process to synthesize graphene on Cu foils
4. Observed Integer Quantum Hall Effect in multiple devices
5. Developed a scalable process to transfer graphene from SiC (000-1) to Pyrex
6. Fabricated gate field effect transistor devices with room temperature operation

Significance:
Our results enable the following outcomes:

1. Established leadership in large-area graphene synthesis on SiC
2. Direct positioning and transferring of graphitic material on relevant substrates
3. Advanced understanding of graphene synthesis on SiC and Cu foil, improving film quality and uniformity
4. Scientific understanding of how domain size/quality depends on growth parameters
5. Improved understanding of electron transport in graphene grown on SiC
6. Advanced fabrication of novel electronic devices that exploit quantum mechanical effects

Although graphene device development is in its infancy, it is widely viewed as having potential major impact to a new generation of electronic devices that may supplant silicon and compound semiconductor electronics in key areas. Major international investment by foreign nations (i.e., China, Singapore) is pursuing graphene materials and device innovation. This external activity creates the threat of technical surprise in the context of economic and national security considerations. Sandia has the opportunity to build upon its present electronic materials and manufacturing strengths, or risk being surpassed by other parties engaged in leading edge graphene materials and device innovation. Hence, this project also more broadly impacts Sandia's S&T reputation as a leader for very high profile graphene materials and device innovation (graphene research was the motivation for the 2010 Nobel Physics prize) and ultracompetitive international research field; as well as, the scientific foundation and vision for enabling leadership in graphene materials and device processing in Microsystems and Engineering Sciences Applications (MESA) as part of a long range goal of positioning Sandia as a "go to" resource for future graphene-based device national security and US economic development needs.

Refereed Communications:

W. Pan, S.W. Howell, A.J. Ross III, T. Ohta, and T.A. Friedmann, "Observation of the Integer Quantum Hall Effect in High Quality, Uniform Wafer-Scale Epitaxial Graphene Films," *Applied Physics Letters*, vol. 97, p. 252101, December 2010.

W. Pan, A.J. Ross III, S.W. Howell, T. Ohta, T.A. Friedmann, and C.T. Liang, "Electron-Electron Interaction in High Quality Epitaxial Graphene," to be published in the *New Journal of Physics*.

L. Biedermann, T. Beechem, A.J. Ross III, T. Ohta, and S. W. Howell, "Electrostatic Transfer of Patterned Epitaxial Graphene from SiC(000-1) to Glass," *New Journal of Physics*, vol. 12, p. 125016, December 2010.

J.K. Lee, S. Kim, M. Points, T. Beechem, T. Ohta, and E. Tutuc, "Magnetotransport Properties of Quasi-Free-Standing Epitaxial Graphene Bilayer on SiC: Evidence for Bernal Stacking," *Nanoletters; Article ASAP*, online, 2010.

J.D. Schmidt, T. Ohta, and T. Beechem, "Strain Carrier Coupling in Epitaxial Graphene," to be published in *Physical Review B*.

Hierarchical Electrode Architectures for Electrical Energy Storage and Conversion
130772

Year 3 of 3
Principal Investigator: K. R. Zavadil

Project Purpose:
Hierarchical electrodes are an enabling technology necessary to produce revolutionary improvements in the performance characteristics of electrochemical devices capable of storing electrical charge (i.e., ultra- or redox capacitors) or interconverting electrical charge and chemical energy (i.e., batteries and reversible fuel cells). Such revolutionary improvements are necessary to ensure a secure energy future for the nation. An important barrier to achieving stable hierarchical electrodes is Ostwald ripening of these nanoscale structures driven by dissolution and redeposition dynamics. As a consequence, constructing stable hierarchical electrodes requires a fundamental understanding of the impact of overall geometric shape, surface energetics, and environmental factors on the dynamics of ripening. We will address the problem of electrode stability by synthesizing novel ripening-resistant structures, exploring the underlying mechanisms of electrochemical-based ripening in these materials, and applying computational methods to develop the necessary understanding of the origins of metastability in accentuated surface area hierarchical electrode structures produced in our synthesis activities. Where ripening is a known degradative mechanism in fuel cell electrocatalysts, synthetic flexibility to design novel forms of active materials backed by a fundamental understanding of the attributes necessary for stability has not been pursued as a strategy to optimize electrode structure and longevity.

Guided by computationally derived insight into materials stability, this project will develop the fundamental knowledge necessary for the creation of stable hierarchical electrode architectures for electrical energy storage and conversion. We will accomplish this goal by applying novel templated synthesis methods to create new structures exhibiting favorable attributes. New computational approaches will be developed to understand surface energetics at the nanoscale. We will develop new diagnostic tools that allow dynamic electrochemical processes to be studied in real time for the important components of the hierarchical electrode structure. The risk inherent in creating material structures with breakthrough performance is offset by the potential impact of enabling revolutionary electrochemical charge and energy storage devices.

Summary of Accomplishments:
A two-step photocatalytic seeding and growth process was discovered and exploited to grow dendritic Pt catalytic nanostructures directly incorporated into hierarchical carbon electrode scaffolds. Molecular dynamics simulations were applied to understand the ripening of dendritic Pt structures possessing positive and negative radius of curvature. Results showed that thermally driven faceting (stress accommodation through slip planes and grain boundary) drives changes in the structure, yet cylindrical holes are maintained below the surface melting temperature due to the presence of negative curvature.

The electrochemical stability of these Pt dendritic structures was confirmed using electrochemical scanning tunneling microscopy. Pt structures can be cycled hundreds of times in an acidic electrolyte to potentials where a surface oxide forms — the first step in a atomic scale dissolution mechanism and ripening — without showing shape change above a 3-nm length scale.

An electrochemical tunneling spectroscopy technique for measuring changes in average charge state as a function of proton and water insertion into ruthenium dioxide, an electrical energy storing material, was demonstrated. This technique allows the dynamics of ion insertion, the energy storage process, to be monitored in real time and creates opportunities for measuring the response, stability, and degradation phenomenon related to the rate at which charge is stored or extracted in ultracapacitor materials coating hierarchical electrode scaffolds.

A new class of opto-electronic and catalytic materials, cooperative binary ionic (CBI) solids, was created. We demonstrated that crystalline CBI solids can be assembled from cationic and anionic porphyrins, determined the resulting crystal structures, and demonstrated that hierarchical mixed CBI nanocomposites can be synthesized. The goal is to produce hybrid CBI nanocomposites in a hierarchical form factor capable of conducting multiple functions such as light harvesting, charge separation and transport, and catalysis necessary for sunlight-driven photosynthesis of carbon-based fuels.

Significance:
This project addresses the DOE mission to provide energy security for our nation. We anticipate impact on ultracapacitor, battery and fuel cell technologies. Revolutionized energy storage capability will enable vehicle electrification allowing for a shift toward domestic fuel sources, point of generation storage facilitating a shift to carbon neutral or renewable energy sources, and expanded flexibility in transmission grid design. The proposed work addresses DHS needs by providing a technology path for miniaturizing power sources for countermeasure sensor architectures.

Refereed Communications:
Y. Song, R.M. Dorin, R.M. Garcia, Q. Li, M.A. Hickner, C.J. Cornelius, J.E. Miller, T. Nwoga, K. Kawahara, W. Li, and J.A. Shelnutt, "Photocatalytic Control of the Growth of Platinum Dendrites on Carbon Supports," to be published in the *Journal of the American Chemical Society*.

Y. Tian, T. Busani, S. Jian, K.E. Martin, F. van Swol, C.J. Medforth, and J.A. Shelnutt, "Hybrid Cooperative Binary Ionic Nanocomposite Materials," to be published in *Advanced Materials*.

Y. Tian, K.E. Martin, J.Y.-T. Shelnutt, L. Evans, T. Busani, J.E. Miller, C.J. Medforth, J.A. Shelnutt, "Morphological Families of Self-Assembled Porphyrin Structures and Their Photosensitization of Hydrogen Generation," *Chemical Communications*, vol. 47, pp. 6069-6071, April 2011.

S.R. Challaa, Y. Song, J.A. Shelnutt, J.E. Miller, and F. van Swol, "Evolution of Dendritic Nanosheets into Durable Holey Sheets: A Lattice Gas Simulation Study," *Journal of Porphyrins and Phthalocyanines*, vol. 15, pp. 449-458, 2011.

Solution Deposited Transparent Conductive Oxides for Nanocomposite Solar Cells
130773

Year 3 of 3
Principal Investigator: P. G. Clem

Project Purpose:
Flexible organic and hybrid inorganic/organic photovoltaic (PV) solar cells require greater long-term reliability and lower cost, transparent conductive oxide (TCO) electrodes to replace indium tin oxide (ITO) for cost-competitive solar energy implementation. Hybrid organic photovoltaics (OPVs), either based on zinc oxide nanorods or carbon nanotubes with polymer or dye-sensitized absorbers, are typically grown on high process temperature (~450 °C) ITO-coated glass substrates. ITO is too expensive for large area hybrid photovoltaic implementation due to indium raw material cost and exceeds the thermal budget for most polymer substrates. We developed transparent conductive oxide films composed of low cost, indium-free materials on polymer substrates, using novel, scalable processing methods and advanced analytical methods to maximize TCO crystallinity, mobility and conductivity.

Previously, solution-processable TCOs were largely incompatible with the organic constituents of an OPV cell; to date, most solution-processed TCOs have required temperatures of over 500 °C to achieve the crystalline order and carrier mobilities required for devices. Our aim was to develop, 1) low substrate temperature processing approaches to TCOs including process temperature (100-400 °C) printable TCO inks, and 2) to use solvothermal reactions to grow crystalline films at 60–90 °C.

Summary of Accomplishments:
In this work, we accomplished our key objectives, including improving the lifetime of organic photovoltaics and developing new, indium-free, low temperature conductive oxide electrodes.

To develop low substrate temperature processing approaches to TCOs, Al_2O_3-ZnO and Ga_2O_3-ZnO transparent conductors were deposited as amorphous layers crystallizable at 300 °C, and processed on polyimide substrates. High-mobility Ga-doped ZnO films on polyimide substrates, such as Kapton, and long-lifetime organic photovoltaic designs were developed toward fully printable, low cost flexible photovoltaics.

Key accomplishments were as follows:

- Developed nano-ZnO/P3HT hybrid solar cells with long operational lifetimes in air.
- Performed one million particle models of organic photovoltaic morphologies to optimize hybrid photovoltaic and organic photovoltaic device architectures. These models enabled new hybrid nanoparticle/organic photovoltaic designs with improved efficiency. We believe that a new hybrid organic photovoltaic that displays long lifetimes even without device encapsulation is a world-first.
- Developed printable conductive oxides on polyimide for organic, CdTe, and copper indium gallium diselenide (CIGS) photovoltaic cells. Both aluminum-doped ZnO and gallium-doped ZnO perform acceptably on polyimide substrates as a result of new solution chemistries and annealing procedures developed.
- Developed reel-to-reel aerosol film printing capability for conductive oxides on polymers. This enables fully printed organic photovoltaic devices with long lifetimes.

Significance:
This project ties to DOE Strategic Plan goals 1.1 energy diversity, 1.2 environmental impacts of energy, 3.1 scientific discovery, and 3.3 research integration. Our research is focused on renewable photovoltaic energy discovery and integration. Development of roll-to-roll processable photovoltaics is a key element for achieving a 20% renewable energy component of the US energy infrastructure. Thin film technologies are the only viable photovoltaic method for this, and the cost of ITO is a limiting factor preventing large-scale PV manufacturing. This research aims squarely at removing this key limitation, while collaborating with ongoing DOE/NREL (National Renewable Energy Laboratory) PV development. There is commercial interest in these developments from flexible photovoltaic companies, which is currently being pursued. In addition, the development of low integration temperature devices has enables several follow-on optical and microelectronics applications not feasible before the research was performed. Follow-on work is continuing with a solar cell manufacturer and through external funding enabled by low-temperature processing.

Refereed Communications:
S.R. Ferreira, P. Lu, Y.J. Lee, R.J. Davis, and J.W.P. Hsu, “Effect of Zinc Oxide Electron Transport Layers on Performance and Shelf Life of Organic Bulk Heterojunction Devices,” *Journal of Physical Chemistry C*, vol. 115, pp. 13471-13475, July 2011.

S.R. Ferreira, R.J. Davis, Y.J. Lee, P. Lu, and J.W.P. Hsu, “Effect of Device Architecture on Hybrid Zinc Oxide Nanoparticle: Poly (3-hexylthiophene) Blend Solar Cell Performance and Stability,” *Organic Electronics*, vol. 12, pp. 1258-1263, July 2011.

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J.Y. Lee, R.J. Davis, M.T. Lloyd, P.P. Provencio, R.P. Prasankumar, and J.W.P. Hsu, “Open-Circuit Voltage Improvement in Hybrid ZnO-Polymer Photovoltaic Devices with Oxide Engineering,” *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 16, pp. 1587-1594, November-December 2010.

High-Temperature, Large Format FPAs for Emerging Infrared Sensing Applications
130774

Year 3 of 3
Principal Investigator: J. K. Kim

Project Purpose:
Current focal-plane array (FPA) technologies based on InSb and HgCdTe material systems have fallen short of meeting larger size, higher operability/producibility, and higher operating temperature requirements of emerging infrared sensing applications. HgCdTe FPAs are limited by the size and quality of CdZnTe substrates on which they are fabricated as well as on intrinsic defects of the material system. On the other hand, the low operating temperature requirement inherent to InSb FPAs is a severe constraint in many applications, despite much better operability and producibility. Accordingly, the size and performance scaling of both technologies have stagnated recently. Our novel n-type-Barrier-n-type (nBn) technology offers a breakthrough solution to these limitations of HgCdTe and InSb.

Summary of Accomplishments:
We have developed a novel FPA technology called "nBn" that addresses these limitations and demonstrated an nBn FPA that outperforms both state-of-the-art HgCdTe and InSb FPAs. In the process, we have gained a comprehensive understanding of the underlying device physics and material science, achieving agreements between theory and experimental results. Novel numerical modeling and experimental processes were developed that add to Sandia's capabilities to make advances in related fields of remote sensing.

Dark currents in InAsSb-absorber nBn devices with a nominal cutoff wavelength of 4.2 μm are now comparable or equal to values described by the empirical Rule-07 trendline of HgCdTe, and the uniformity of nBn FPAs significantly exceeds that of HgCdTe, with comparable spectral bandwidth and quantum efficiency. We have investigated device design parameters both experimentally and theoretically, using a predictive 2D numerical model to understand their effects on device characteristics. In devices with barriers that are not intentionally doped, absorber doping plays a dominant role in the carrier lifetime, dark current, and operating voltage. Minority carrier hole lifetimes have been measured optically and compared to values extracted from model fits to dark current data. We have also made FPAs from optimized nBn structures, measured dark and photocurrent distributions, and compared them to HgCdTe FPAs. Defective pixels are randomly distributed, with defect clusters no larger than four pixels. Most notably, the "hot tail" of the dark current distribution is absent in our nBn FPAs, which allows them to be operated at 10 to 20 Kelvin higher in temperature than HgCdTe.

Significance:
Success will expand the fundamental knowledge of this novel material system, establish key numerical and experimental capabilities that Sandia currently lacks, and establish an FPA project that will deliver far-reaching, differentiating technologies for Sandia's remote sensing projects. Air Force Research Lab, Army Night Vision Electronic Sensors Directorate, Defense Advanced Research Projects Agency, and others have shown interest in fielding this technology.

Narrow-Linewidth VCSELs for Atomic Microsystems
130775

Year 3 of 3
Principal Investigator: D. K. Serkland

Project Purpose:
Vertical-cavity surface-emitting lasers (VCSELs) are well suited for emerging photonic microsystems due to their low power consumption, ease of integration with other optical components, and single frequency operation. However, the typical VCSEL linewidth of 100 MHz is approximately ten times wider than the natural linewidth of atoms used in atomic beam clocks and trapped atom research, which degrades or completely destroys performance in those systems.

The purpose of this project is to reduce VCSEL linewidths below 10 MHz to meet the needs of advanced sub-Doppler atomic microsystems, such as primary frequency standards and atom traps. In order to reduce the VCSEL linewidth, one must simultaneously increase the quality factor of the laser cavity and decrease the linewidth enhancement factor of the active region. We intend to increase the stored optical energy and thus cavity quality factor by extending the cavity length to 30 microns (over 10 times longer than normal), terminating the extended cavity with an external high-reflectivity dielectric mirror. The 10-fold increase in cavity length precludes an all-semiconductor structure, but is still small enough to permit wafer-scale microfabrication of the device. Significant metal organic chemical vapor deposition (MOCVD) epitaxial growth development will be undertaken to allow the extended cavity geometry, minimize free-carrier absorption losses, and develop active quantum wells that achieve minimum linewidth enhancement (alpha) factor. VCSELs have long been a differentiating technology for Sandia, due to the complexity of VCSEL design, epitaxial growth, and microfabrication. Success in wafer-scale fabrication of narrow-linewidth VCSELs could enable significant follow-on work to tailor these devices for use in specific high-performance atomic-physics microsystems.

Summary of Accomplishments:
We succeeded in our goal to reduce VCSEL linewidths below 10 MHz to meet the needs of emerging sub-Doppler atomic microsystems, such as cold-atom traps. We investigated two complementary approaches to reduce VCSEL linewidth: increasing the laser-cavity quality factor, and decreasing the linewidth enhancement factor (alpha) of the optical gain medium. We developed two new VCSEL devices that achieved increased cavity quality factors: 1) all-semiconductor extended-cavity (EC) VCSELs, and 2) micro-external-cavity surface-emitting lasers (MECSELs). The EC-VCSEL device achieved a five-fold reduction in VCSEL linewidth (from 50 to 8.5 MHz) primarily by adding cavity length extension layers to a standard oxide-confined 850-nm VCSEL structure.

The newly developed MECSEL device utilized wafer-scale semiconductor microfabrication techniques to produce thousands of external-cavity lasers on a single GaAs wafer. The MECSEL fabrication process produced a microscopic curved dielectric mirror above each VCSEL device on the GaAs wafer. We demonstrated a MECSEL device that exhibited a threshold current of 2.1 mA, a differential quantum efficiency of 41%, and operated in a single polarization, transverse, and longitudinal mode up to thermal rollover at an output power of 2 mW. The additional cavity length of the MECSEL, relative to a VCSEL, is expected to enable higher output powers and narrower linewidths.

Finally, we investigated, both experimentally and theoretically, the linewidth enhancement factor of VCSEL gain regions. We learned from the theoretical models that the barrier layers contribute significantly to linewidth enhancement, and we started development of a new and more accurate model that will compute the linewidth enhancement factor of an entire gain region including many-body effects.

The new VCSEL devices have demonstrated linewidths below 10 MHz, and linewidths below 1 MHz seem feasible with further optimization.

Significance:
Sandia's differentiating capabilities in compound semiconductor epitaxial growth, VCSEL microfabrication, and optical microsystem integration were enhanced by this research project. Success in making a narrow-linewidth VCSEL could generate significant follow-on work in a variety of areas: primary frequency standards, neutral atom and ion traps, and quantum information research. Applications range from improved military communication and navigation to quantum encryption.

Phonon Manipulation with Phononic Crystals
130777

Year 3 of 3
Principal Investigator: I. F. El-Kady

Project Purpose:
We proposed a fundamental understanding of, and a methodology for, deterministic phonon spectrum control at terahertz (THz) frequencies (100 K-phonons) using a top-down phononic crystal (PnC) approach. The objective here was to demonstrate the at-will control of thermal phonons, and the ability to mold and change a material's thermal properties via PnC structures enabling new classes of thermal and ultra/hypersonic devices. Alternative approaches to phonon control are based on surface texturing to increase phonon scattering or shrinking the diameter of the material to prevent bulk propagation much like waveguide cutoff, or phonon scattering off grain boundaries. All such approaches are either highly nondeterministic or are capable of only targeting a narrow spectral range. In contrast, PnCs utilize physics similar to Bragg scattering. In a fashion reminiscent of photonic lattices, spectrally wide bandgaps can be deterministically produced in which phonons are inhibited, accompanied by redistribution of the phononic density of states (DOS). This offers a unique vehicle for tailoring the phonon spectrum for numerous applications and awards a larger degree of control. For example, by selectively enhancing the efficiency of phonon propagation in specific spectral bandwidths, enhanced thermal-to-radio frequency tags and micro-coolers can be realized. Conversely, by selectively suppressing and or impeding the propagation of THz phononic spectral bands, exceptionally high thermoelectric figure of merit (ZT) materials can be achieved. Furthermore, other important processes, such as the electron-phonon interactions that cap the performance in Hi-TC superconductors, and phonon-photon interactions essential for quantum-well or quantum-dot based solid state lighting could potentially be impacted by the profound control provided by PnCs. If successful, this approach will lead to new thermal applications such as efficient and directional heat removal from integrated circuits, high efficiency thermoelectric materials, and new approaches to thermal harvesting. Finally, this project will lay the foundation for realizing the first phononic metamaterials, essential for high-precision focusing, ultrasonic imaging devices, and deep-sea cloaking.

Summary of Accomplishments:
In the theoretical area, we were able to extend our 2D model to 3D and account for the actual thickness of the PnC. We were further able to incorporate hybridized lattice geometries into the model. This allowed us to evaluate the density of states and from it estimate the reduction in thermal conductivity due to a PnC. The result was a 98% reduction in silicon thermal conductivity at less than 20% porosity, which we attributed to the anomalous dispersion of the PnC, especially the existence of flat dispersionless bands and negative or backward scattering bands. This result was validated via time-domain thermal reflectance measurements, which enable us to measure the phonon lifetimes and deduce the thermal conductivity of the sample. These results indicate that we may be able to realize record-breaking ZT in silicon at room temperature. To validate this, we performed direct electrical and thermal conductivity measurements on actual samples by integrated serpentine heaters and temperature sensors with the current PnCs in the Microsystems and Engineering Sciences Applications (MESA) fabrication facility. The resulting data confirmed a reduction in thermal conductivity greater than the porosity factor, with a simultaneous reduction in electrical conductivity of no more than the porosity factor. Furthermore, our collaborators at the University of New Mexico have also developed focused ion beam fabrication techniques capable of producing high quality PnC lattices with operating frequencies as high as 3THz. We have also fabricated and measured the thermal conductivity of both square and hexagonal lattice PnCs to fully discriminate (for the first time) harmonic versus inharmonic phonon scattering effects by comparing PnC samples with identical porosities and limiting dimensions (incoherent

scattering) but different lattice topologies (coherent scattering). These results combine for an estimated factor of 2 increase in ZT over the bulk Si value for in-plane operation, and a factor of 5 increase cross-plane.

Significance:
This research could result in a new class of thermal materials for heat control and thermal energy scavenging thermoelectric cooling. Evidence thus far suggests that we are on the path of realizing ZT=5 in silicon, which would revolutionize thermal energy scavenging. This research will also lay the foundation for realizing the first phononic metamaterials essential for high-precision focusing and manipulation of vibrational energy for a wide range of ultrasonic imaging devices and deep-sea cloaking. Furthermore, it promises to put Sandia at the forefront of a new branch of science of direct interest to DOE and DoD. Specific near-future applications that could be enabled by this technology include improved sensor cooling and reduced size, weight and power (SWAP) requirements for satellite applications, high-temperature thermal scavenging in hypervelocity aircraft, and improved thermal masking and waste heat recovery for military vehicles similar to the BAE ADAPTIV™ system.

Refereed Communications:
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P.E. Hopkins, C.M. Reinke, M.F. Su, R.H. Olsson, E.A. Shaner, Z.C. Leseman, J.R. Serrano, L.M. Phinney, and I. El-Kady, "Reduction in the Thermal Conductivity of Single Crystalline Silicon by Phononic Crystal Patterning," *Nano Letters*, vol. 11, pp. 107-112, January 2011.

Y.M. Soliman, M.F. Su, Z.C. Leseman, C.M. Reinke, I. El-Kady, and R.H. Olsson III, "Effects of Release Holes on Microscale Solid-Solid Phononic Crystals," *Applied Physics Letters*, vol. 97, p. 081907, August 2010.

Y.M. Soliman, M.F. Su, Z.C. Leseman, C.M. Reinke, I. El-Kady, and R.H. Olsson III, "Phononic Crystals Operating in the Gigahertz Range with Extremely Wide Band Gaps," *Applied Physics Letters*, vol. 97, p. 193502, November 2010.

C.M. Reinke, M.F. Su, R.H. Olsson III, and I. El-Kady, "Realization of Optimal Bandgaps in Solid-Solid, Solid-Air, and Hybrid Solid-Air-Solid Phononic Crystal Slabs," *Applied Physics Letters*, vol. 98, p. 061912, February 2011.

Real-Time Studies of Battery Electrochemical Reactions Inside a Transmission Electron Microscope
130778

Year 3 of 3
Principal Investigator: J. P. Sullivan

Project Purpose:
The purpose of this project is to develop new capabilities to measure and understand electrochemical mechanisms in electrochemical energy storage systems (batteries). This project is motivated by the global need to improve the energy density, power density, and reliability of energy storage systems in order to meet goals for the expansion of green energy technologies. Given their high gravimetric energy density and good reversibility, Li-ion cells have received some of the greatest interest, but there are key scientific challenges related to the capacity and lifetime of the cathodes and anodes, degradation after cycling, and high-temperature stability. The fundamental study of electrochemical phenomena in this system has been hampered by the great lack of experimental and theoretical techniques that can identify structural changes in battery materials with atomic to nanoscale resolution during actual battery operation. The objective of this project is to investigate Li-ion battery electrochemical processes in real time inside a transmission electron microscope (TEM), using 1) a novel sealed silicon micromachined fluidic platform and 2) a simple open platform using a vacuum-stable ionic liquid (IL) electrolyte. These platforms are used to measure structural changes within and at the surfaces of anodes and cathodes that result from Li insertion and de-insertion. In situ studies are used to identify the strain accommodation mechanism in conversion anodes, the Li ion diffusion kinetics in conversion and alloying anodes, and the role of surface passive oxide layers that simulate the solid-electrolyte-interphase (SEI). We also use molecular dynamics (MD) and ab initio MD (AIMD) to model the formation of SEI compounds on carbon-based and Li anodes and to understand the reaction products that form during electrolyte reduction across a barrier layer simulating a thick SEI film. The outcome of the project is the delivery of new techniques to study electrochemical reactions and the generation of understanding of electrochemical mechanisms at the atomic scale.

Summary of Accomplishments:
Significant advances were made in several areas related to understanding Li-ion battery electrochemistry. First, we successfully developed a versatile and powerful approach to measuring Li-ion battery electrochemical reactions in real-time with atomic scale resolution inside a TEM. This capability uses a nanomanipulator inside the TEM to assemble an electrochemical cell consisting of battery materials (e.g., tin oxide, silicon, zinc oxide, and aluminum anode nanoparticles and nanowires), a Li-containing counter electrode (Li or Li cobalt oxide), and an ionic liquid electrolyte. After cell assembly, we identified several remarkable electrochemical mechanisms associated with anode lithiation and delithiation. We identified the strain accommodation mechanisms in conversion anodes, identifying new behavior such as a dislocation-induced amorphization of the crystalline anode phase. We also observed diffusion anisotropy in silicon anodes and identified the role of electrical conductivity in influencing the silicon lithiation rate. We identified failure mechanisms associated with cracking in silicon and the quite different mechanism of vacancy coalescence and void formation in the related material, germanium. In addition, we observed that thin aluminum oxide layers that are used to create an artificial SEI layer react with Li and act as an effective solid electrolyte, providing a conduit for lithiation of the underlying material. In addition to this in situ platform, we developed a chip-based platform for single particle electrochemistry and a revolutionary new microelectromechanical system (MEMS)-based liquid cell platform for in situ TEM that permits the study of electrochemistry inside a TEM using conventional electrolytes. Lastly, we developed ab initio molecular dynamics (AIMD) techniques to identify the chemical reaction mechanisms associated with the initial and late stages of

SEI formation. We identified a new, unrecognized reaction mechanism that leads to CO formation during initial SEI formation; whereas at later stages, we identify that the di-carbonate reaction product dominates.

Significance:
This work has led to the development of a new capability in the area of electrochemical energy storage, a capability that enables one to view and understand electrochemical reactions in real-time with atomic scale resolution. In addition, we developed sophisticated MEMS-based electrochemical cells that permit an even greater variety of electrochemical reactions to be observed inside a TEM, specifically electrochemical reactions involving common electrolytes, such as water or ethylene carbonate mixtures, which normally cannot be used in the vacuum environment of the TEM. Equally importantly, we developed sophisticated modeling techniques based on AIMD that permit the identification and prediction of reaction products that form at electrode-electrolyte interfaces. Using these capabilities, we have identified important electrochemical reaction mechanisms in Li-ion battery materials as they lithiate and delithiate and interfacial reactions between ethylene carbonate electrolytes and Li-ion battery anode phases. This work leads to important suggestions on how to improve the performance and lifetime of Li-ion batteries. This is important for meeting DOE goals in advancing the use of clean energy technologies. At Sandia, this project has led to the creation of a strategic area of excellence in in situ characterization for batteries. This work is an important part of Sandia's Energy Storage Roadmap and has led to new funded initiatives that aim to use the capabilities developed in this project for understanding the mechanisms of battery degradation.

Refereed Communications:
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X.H. Liu, H. Zheng, L. Zhong, S. Huang, K. Karki, L.Q. Zhang, Y. Liu, A. Kushima, W.T. Liang, J.W. Wang, J.-H. Cho, E. Epstein, S.T. Picraux, T. Zhu, J. Li, J.P. Sullivan, J. Cummings, C. Wang, S.X. Mao, Z.Z. Ye, S. Zhang, and J.Y. Huang, "Anisotropic Swelling and Fracture of Silicon Nanowires During Lithiation," to be published in *Nano Letters*.

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X.H. Liu and J.Y. Huang, "In Situ TEM Electrochemistry of Anode Materials in Lithium Ion Batteries," to be published in *Engineering Environmental Science*.

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Science-Based Solutions to Achieve High-Performance Deep-UV Laser Diodes
130779

Year 3 of 3
Principal Investigator: M. H. Crawford

Project Purpose:
A number of mission-critical applications would greatly benefit from a compact, deep-ultraviolet (UV) (< 340 nm) laser diode (LD); however, commercial LDs are currently limited to longer UV wavelengths. AlGaN semiconductor alloys are the most promising materials for deep UV LDs, with potential for emission across the 200–365 nm region. To date, realization of deep UV LDs has been thwarted by the lack of fundamental insight and solutions to key AlGaN materials challenges. These challenges include 1) nanoscale point defects, 2) p-doping limitations, and 3) high internal optical losses and limitations to optical gain.

We propose a science-based approach that will apply our state-of-the-art AlGaN metal-organic vapor-phase epitaxy capabilities, innovative materials growth and heterostructure design strategies, differentiating materials characterization techniques, and advanced device modeling to gain fundamental insight into these three important challenges. In this project, we will apply those insights and Microsystems and Engineering Sciences Applications (MESA) microfabrication processing capabilities to design and fabricate AlGaN LDs in the 300–340 nm region. If successful, our project will yield the shortest wavelength deep-UV LDs to date, relevant to a range of applications including fluorescence-based bioagent sensing. Materials insights gained from this project could be applied to a range of III-Nitride materials and devices, enabling advances in deep UV light emitting diodes (LEDs) for water purification, visible LEDs for solid-state lighting, and InGaN solar photovoltaics. This project, therefore, offers an opportunity to leverage Sandia strengths and achieve both science and technology breakthroughs with strong relevance to DOE missions.

Summary of Accomplishments:
Highlights of accomplishments over the life of the project include both materials and device advances. To understand potential limitations to AlGaN materials quality and performance, we performed studies to quantify the properties and impact of crystalline defects in constituent layers of AlGaN laser heterostructures, including quantum well (QW) active layers and doped cladding layers. We combined deep-level optical spectroscopy and photoluminescence to investigate how QW growth temperature mediates the interplay between defect incorporation and luminescence efficiency. Our studies revealed three distinct deep levels in AlGaN quantum wells and a quantitative correlation between increased growth temperatures, reduced density of all observed deep levels, and enhanced luminescence efficiency. A second effort explored solutions to the high densities of non-radiative dislocations in AlGaN-on-sapphire templates. We developed a novel growth approach that resulted in greater than 10x reduction of threading dislocations and greater than 7x enhancement of AlGaN QW luminescence. As a third effort, we explored development of p-type short-period superlattices as an approach to achieve more effective p-type conduction in cladding layers needed for shorter-wavelength laser demonstrations. As a fourth effort, we developed a method for achieving etched AlGaN facets with verticality and smoothness needed for laser applications. We further demonstrated high reflectivity facet coatings with greater than 90% reflectivity at relevant UV wavelengths. Finally, we combined the extensive materials and processing developments into packaged ridge waveguide laser heterostructures and conducted testing of electrical and optical performance.

Significance:
Fundamental insights into the key topics of point defects, low dislocation substrates and p-type doping could be applied to the vast III-Nitride family of materials and devices, enabling advances in LEDs for solid-state lighting, InGaN solar photovoltaics, AlGaN/GaN high-electron-mobility-transistors and other devices of relevance to Sandia missions. The extensive materials and processing advances and related progress toward deep UV laser diodes will be leveraged in a new internal project supporting a particular Sandia mission area. Key materials advances achieved in this project have been published in refereed journals, thus benefitting the technical community. Etching processes developed in this project for laser diode facets have already been applied to the benefit of other Sandia projects. For example, this process is now used to achieve high quality InGaN nanostructures in support of Sandia's Solid State Lighting Science Energy Frontier Research Center, funded by the US DOE Office of Basic Energy Sciences.

Refereed Communications:
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Mechanisms for Charge Transfer Processes at Electrode-Solid-Electrolyte Interfaces
130780

Year 3 of 3
Principal Investigator: K. F. McCarty

Project Purpose:
The purpose of this project is to develop and apply new in situ spectroscopies to understand and improve electric charge transfer in electrochemical devices such as fuel cells and batteries. Electrochemical technology will play an increasing role in meeting the nation's energy challenges in both stationary power applications and transportation. Current fuel cells and batteries are inferior to combustion technologies in terms of performance and reliability. The essential physical phenomenon occurring in all electrochemical devices is the transfer of electrical charge across material interfaces. How this charge transfer occurs and its relationship to the device's performance and reliability is largely unknown, in part, because few techniques exist that can characterize the charge transfer at a fundamental level as it occurs. This project develops fundamental understanding of interfacial charge transfer by characterizing it during electrochemical operation. We are developing the technique of ambient-pressure x-ray photoelectron spectroscopy to study charge transfer at realistic pressures and temperatures in fuel cells and batteries. The technique measures the electrical potentials across the device's interfaces, determines the chemical nature of the surface adsorbates and characterizes the material phases present during operation. We are also using micro and nanofabrication to develop a new experimental "platform" with accessible surfaces and enhanced performance. We realized that soft x-ray diagnostics could be applied to study electrochemical processes as they occur. More specifically, we are the first group to use ambient-pressure x-ray photoelectron spectroscopy to study electrochemical devices are they operate. This project was the appropriate route to evaluate our method, which had several large risks.

Summary of Accomplishments:
In this project, we developed a substantially more powerful method to understand electrochemistry that involves gas-phase molecules reacting with solid surfaces. Our approach uses x-rays to provide chemical characterization of the solid materials and their adsorbates. It also determines the local electric potential, information vital to fully measuring the electrochemical potential in devices. The most important attribute of our approach is that the x-ray characterization is performed *in-operando*, that is, as electrons and ions flow through a device with a solid-state electrolyte. Our specific accomplishments include the following: 1) the design of a simple yet powerful fixture to heat and apply biases to solid-state electrolytes in a traditional surface-science vacuum chamber; 2) developing a method that uses photoelectrons for the non-contact measurement of local electric potential; 3) the first spectroscopic identification of electrochemical reaction intermediates on a solid-oxide electrolyte; 4) extending the approach to batteries by characterizing the phases that store charge after electrochemical oxidation; 5) designing and building a sophisticated apparatus that performs x-ray characterization of a ion-conducting membrane that separates two gas environments; and 6) using the two-environment apparatus to understand the chemical origin of why cation substitution affects electrocatalytic activity of state-of-the-art perovskite-structure materials. Our approach is ready to be applied to improve the efficiency, reliability and affordability of electrochemical devices such as fuel cells, electrolyzers and the types of batteries that involve solid/gas reactions (such as lithium air batteries).

Significance:
This work is directly relevant to DOE's mission of providing the science and technology to power the US without contributing to climate change. This project is developing new ways to characterize the electrochemical technologies that will be increasingly relied upon to achieve energy security by efficiently storing and converting energy.

Refereed Communications:
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C. Zhang, M.E. Grass, A.H. McDaniel, S.C. DeCaluwe, F. El Gabaly, Z. Liu, K.F. McCarty, R.L. Farrow, M.A. Linne, Z. Hussain, G.S. Jackson, H. Bluhm and B.W. Eichhorn, "Measuring Fundamental Properties in Operating Solid Oxide Electrochemical Cells by Using In Situ X-ray Photoelectron Spectroscopy," *Nature Materials*, vol. 9, pp. 944-949, September 2010.

S.C. DeCaluwe, M.E. Grass, C.J. Zhang, F. El Gabaly, H. Bluhm, Z. Liu, G.S. Jackson, A.H. McDaniel, K.F. McCarty, R.L. Farrow, M.A. Linne, Z. Hussain and B.W. Eichhorn, "In Situ Characterization of Ceria Oxidation States in High-Temperature Electrochemical Cells with Ambient Pressure XPS," *Journal of Physical Chemistry C*, vol. 114, pp. 19853-19861, November 2010.

F. El Gabaly, M.E. Grass, A.H. McDaniel, R.L. Farrow, M.A. Linne, Z. Hussain, H. Bluhm, Z. Liu and K.F. McCarty, "Measuring Individual Overpotentials in an Operating Solid-Oxide Electrochemical Cell," *Physical Chemistry Chemical Physics*, vol. 12, pp. 12138-12145 August 2010.

Calculations of Charge Carrier Mobility and Development of a New Class of Radiation Sensors for Real-Time 3D Source Location
141512

Year 2 of 3
Principal Investigator: M. S. Derzon

Project Purpose:
This project responds to the call for advanced gamma sensors in the areas of Special Nuclear Material (SNM) detection, all things nuclear, and space science. The S&T question is how do we extract more of the information carried in a SNM quantum (gamma or neutron) than is currently possible? The challenge is to perform spectroscopy, identify the mechanism of interaction, to follow a track in order to obtain incident photon direction. Our goal is to determine gamma interaction type (Compton, photoelectron and pair-production) and the limits on interpretation of deposited energy and direction. Benefits to the users will be vastly decreased time to detect, identify, and locate a radioactive source compared with traditional bulk radiation detectors. The science of this project is focused on the discovery and utilization of the basic signal collection processes (nanoscale) for track following across embedded pixels.

This is a difficult problem, and we have not yet even made a single pixel. It has not been deemed credible to propose a method that might lead to a million pixels. Our end goals are: 1) to have built and tested a few pixels fabricated in a simple 3D structure and 2) to mature the modeling and determine if the benefits hypothesized are indeed possible. Ron Kensek (unpublished) showed that the source direction can be converged upon very rapidly. Under this project, we will examine how well this analysis holds up by relaxing both of the above assumptions and pixelating a potential system to clarify the requirements. We will fabricate preamplifiers and amplifiers in the wafer epilayer to reduce electronics volume and use the handle layer to hold the sensor material; this has never been done before in a monolithic process.

Summary of Accomplishments:
We completed the design and initial bench testing of an application-specific integrated circuit (ASIC), which contains a single pixel preamp and shaper amplifier. 80 e-noise was obtained in bench testing; this is excellent agreement with the circuit model. The base pixel circuit and shaper occupy ~300 micron x 300 micron wafer area. This is important because the per pixel electronics is roughly the per-pixel sensor area. It is important that the electronics be smaller than the pixel size for scaling purposes.

We liquefied xenon in a 10-wafer sandwich configuration and obtained preliminary spectra. This must be repeated once our ASIC is adapted to the sensor. The spectra are currently being modeled again for the physical configuration of the experiment as performed. This was different than the original design. The count rate obtained showed that the sensor is sensitive well below rates currently used for dosimetry and the results of these experiments helped us realize that this technology is a large advance in rate meter/dosimeter technology. The smaller pixels of the experiment have been modeled and compared to the experimental results. We have bonded Si-wafers in a two-layer sandwich and increased the failure stress from ~200 psi to over 1200 psi. This is quoted in this way because failure did not occur at the bond. The failure occurred at the epoxy joint holding the bonded sample in the tensile tester. These experiments met all major milestones.

Significance:
These concepts will dramatically illustrate how the microsystems and engineering sciences applications project improves the ability of the DOE, NNSA, DHS and DoD to meet a number of NNSA/DOE/DoD/Sandia missions. There is a significant need to rapidly identify and locate ionizing radiation from x-ray, neutron and gamma sources for SNM detection. Bringing together Sandia's

microsystem and integration capabilities to address this national security issue, this project illustrates Sandia's role as a leader in transformational radiation detection research. These concepts offer numerous benefits over current detection technology for our missions in defense, counterproliferation and weapons of mass destruction detection. The work enables fully 3D microelectronic devices for terrestrial and space-based missions.

An example of the value of this work has already been demonstrated. In the small volume liquid Xe sensing data that we acquired in the lab, we observed the presence of a radiation source just a few times brighter than natural background in the course of a few minutes. This was in a simple device that could be made low power, acts as a rate-meter and dosimeter, could have very simple electronics and no need for photon counting. We have already had commercial interest and expect to test a larger version of the same device as a spectrometer in the next year. We have used these results as the basis for suggesting a replacement for the combined x-ray diagnostic currently fielded in by National Aeronautics and Space Administration (NASA) that is ending its useful life.

Chirality-Controlled Growth of Single-Walled Carbon Nanotubes
141513

Year 2 of 3
Principal Investigator: S. M. Dirk

Project Purpose:
Single wall carbon nanotubes (SWNT) may be the most promising material to achieve game-changing impacts for future nanosystems and computing in the next decade. Much of the excitement surrounding SWNTs is their ability to be either semiconducting or ballistic conductors based on their individual crystalline structure, or chirality. SWNTs consist of a single rolled sheet of graphene; rolling along different lattice vector lines produces SWNTs with differing chirality and diameter, each with its own unique electrical properties. All known synthetic methods produce SWNTs in mixtures of semiconducting and conducting types. Typical chemical vapor deposition (CVD) processes, such as the Rice University HiPCO method, simultaneously produce 80 different SWNT chiralities, where two-thirds are semiconducting, each with a different bandgap. Great efforts have been made to produce SWNT batches that are primarily semiconducting with narrow chirality distributions, most using post-growth chemical separation techniques. Separation methods, however, do not address the manner in which SWNTs of a given chirality may be placed onto a microchip. Therefore, even a successful chemical isolation of a given SWNT chirality will be difficult to implement in next-generation nanoelectronics.

This project seeks to develop methods to grow SWNTs with a given chirality (or bandgap) directly on Si substrates exactly where they are needed, using a process that is ultimately compatible with microelectronics processing. We hypothesize that appropriate control of the reaction conditions will change the growth of SWNTs from a kinetic to a thermodynamically controlled process, resulting in high yields of specific SWNT chiralities. In addition, we propose to study the novel use of nanopore zeolite scaffolds as templates for SWNT growth that provide precise steric limitations to within tenths of angstroms for SWNT diameters. The resulting combination of these unique approaches may lead to the growth of specific chiral SWNTs located at precisely the right location.

Summary of Accomplishments:
In order to accomplish the controlled chiral growth of single-walled carbon nanotubes (SWNTs), work needed to be completed on a number of areas including template growth, catalyst precursor development, nanotube growth, and nanotube characterization. We have synthesized zeolites including Mordenite Framework Inverted (MFI) type (0.55 nm pores) in addition to mesoporous silica (3–4 nm pores). We have developed a number of solution-based catalyst deposition processes. We have demonstrated a growth technique that enables SWNT growth on silicon substrates, which have been coated with a tungsten barrier layer prior to nickel catalyst deposition in order to prevent Ni silicide formation. The new SWNT growth technique enables growth at temperatures as low as 350 °C, which is very silicon fabrication facility (Fab) friendly. Low temperature growth (350–490 °C) provides some control of nanotube diameter; however, the control is not as great as the control observed at higher temperature (530–630 °C) previously reported by our group (Siegal, et al., *J. Phys. Chem. C.*, 2010, 114, 14864.).

In an effort to further control chirality, we have combined the templates (mesoporous silica) which with high temperature carbon nanotube (CNT) growth (600 °C). We have observed and characterized CNT growth in the presence of the templates with the use of both scanning electron microscopy (SEM) and Raman spectroscopy, however, the zeolite thin film templates cracked and delaminated under the high-temperature growth conditions. To solve these template/substrate problems, we have been growing large zeolite single crystals (millimeter scale). The single crystals will be used as both template and substrate and will not be exposed to the same stresses as the thin film (<100 nm) templates, which should solve the cracking and delaminating problems. In addition, we have begun to explore the use of anodized aluminum oxide (AAO) free standing nanoporous membranes combined with atomic layer deposition (ALD) as templates for controlled SWNT growth.

Significance:
Sandia is currently engaged in researching next-generation microelectronics, energy production technologies, defense applications, and intelligence applications. SWNTs offer unique properties that, if taken advantage, will enable more efficient energy collection systems, faster microelectronics, and smaller sensors. This research will provide Sandia with a game-changing core technology that will benefit DOE, NNSA, DoD and other national security agencies.

Several key accomplishments have been realized during FY 2011, including demonstration of carbon nanotube (CNT) growth at temperatures as low as 350 °C which is almost a 200 °C lower growth temperature than we demonstrated in FY 2010. The extremely low CNT growth temperature will enable growth within the silicon fabrication facility. This technology advance will enable the fabrication of very small vias and novel CNT transistors.

We have combined the templates (mesoporous silica) with high-temperature CNT growth (600 °C), which is an important advance to control nanotube chirality. To date, we have not achieved chirality control and have noted that the zeolite thin film templates cracked and delaminated under the high-temperature growth conditions. To solve these template/substrate problems, we have been growing large zeolite single crystals (millimeter scale). The single crystals will be used as both template and substrate and will not be exposed to the same stresses as the thin film (<100 nm) templates, which should solve the cracking and delaminating problems. In addition, we have begun to explore the use of AAO freestanding nanoporous membranes combined with ALD as templates for controlled SWNT growth. Both new template approaches should provide much better templates for controlled SWNT growth.

Development of Electron Nano-Probe Technique for Structural Analysis of Nanoparticles and Amorphous Thin Films
141514

Year 2 of 3
Principal Investigator: P. Lu

Project Purpose:
Nanoparticles (NPs) and amorphous thin films are of great interest for basic science and energy related research at DOE. The lack of long-range order in these NPs (<5nm, crystalline or amorphous) and in amorphous materials makes structural characterization techniques based on traditional diffraction, such as electron and x-ray diffraction, no longer useful. To describe the atomic-level structure of these nanomaterials, a pair distribution function (PDF) is often used which describes the local atomic structure in terms of neighboring distances and coordination numbers. Current PDF analysis techniques are based on x-ray or neutron scattering and extended x-ray absorption fine structure (EXAFS). While these techniques are capable of providing PDF analysis for nanoscale materials, they lack the spatial resolution required for analyzing complex materials and devices, require relatively large amounts of material, and usually require large, limited-access facilities such as neutron scattering centers and synchrotron x-ray sources.

We are developing two transmission electron microscope (TEM) electron-based analogues to x-ray/neutron-based PDF and EXAFS capabilities. The key advantages of electron-based PDF include high spatial resolution (<1 nm), structural mapping capability, limited demands on the materials (a few particles), and readily available access to the researcher. Several novel approaches are being developed in the project which will allow us to overcome technical difficulties associated with analyzing electron scattering data. The approaches include: 1) collecting spectrum-image (SI) electron scattering datasets in scanning TEM (STEM) mode, and analyzing the datasets using a multivariate statistical analysis (MVSA) approach, and 2) integrating reverse Monte Carlo (RMC) molecular structural modeling with structure determination. We will apply these newly developed techniques to study fundamental materials phenomena in metal oxides and semiconducting polymers. The new PDF method will provide an essential capability to characterize NPs and amorphous thin films, crucial for the advancement of nano-science research and technology development. To our knowledge, the approaches in this project have not been reported in the literature.

Summary of Accomplishments:
We have made several key accomplishments, including the following: 1) establishment of theory and computer codes to perform PDF analysis on electron scattering patterns, as well as the extended energy loss fine structure (EXELFS) of electron energy loss spectra (EELS); 2) molecular dynamics (MD) structural modeling of Au and ZnO NPs, and using the combined experimental and theoretical results of the Au NPs to confirm the PDF analysis and understand new physical phenomena; 3) establishment of the experimental conditions for STEM nano-scattering pattern (NSP) spectral image (SI) data collection and EELS SI data collection; 4) demonstrating structural recognition and mapping capability based on both the NSP-SI technique and the EELS-SI technique by using MVSA; 5) conducting PDF analysis on Au NPs and amorphous SiO using x-ray scattering PDF analysis to establish the equivalency between electron scattering and x-ray scattering based PDF techniques. Significant progress has been made toward the technical milestones. We have met most milestones in Goal 1 (Establish the PDF capability), and all milestones in Goal 2 (Qualify the PDF) and Goal 3 (Establish the PDF spatial mapping capability). Milestones in Goal 1 (G1ME, G1MG and G1MH), related to the RMC molecular structural modeling, however, have not been met due to staff changes and technical difficulties in extending molecular structure modeling to more general, complex materials systems. Molecular structure modeling

was originally included to overcome the expected strong dynamic effect of electron scattering in thick TEM specimen. The work so far, however, indicates the effect on electron scattering PDF analysis is quite limited. We expect that the result of not meeting these milestones in Goal 1 will have little impact on the overall objectives of our project.

The success of project has led to five publications (submitted or in submission).

Significance:
The success of this project will provide DOE with an ability to characterize the structure of nanoscale and amorphous materials and will impact DOE missions in contributing to key national efforts such as Energy and Energy transport, and Homeland Security and Defense (HSD). Research projects in NPs and amorphous thin films are closely related to applications in renewable energy sources, energy storage, and alternative fuel technologies. This project directly addresses technical needs for these projects. In addition, these techniques could be applied to identification and understanding of thin film corrosion products which are of importance to nuclear weapons projects.

Dynamically and Continuously Tunable Infrared Photodetector Using Carbon Nanotubes
141515

Year 2 of 3
Principal Investigator: F. Léonard

Project Purpose:
Infrared photodetectors play a key role across Sandia mission areas being used, for example, in space-based surveillance, thermal imaging, aerial surveillance, and nondestructive imaging of components. Infrared (IR) detectors rely on pixel arrays, each pixel having a dimension in the ten to twenty micron range. Pixels are often made of exotic semiconductors like $Hg_{1-x}Cd_xTe$ because the bandgap (and thus the sensitivity to different optical wavelengths) can be controlled by varying the composition x. However, once a composition is chosen, this fixes the sensitivity to a specific range of wavelengths leading to black-and-white detection. As everyday experience with human vision shows, color detection improves discrimination significantly, and the same applies to IR detectors. Thus one important need is dynamic multiwavelength detection in the IR. Current technology achieves two-color detection at the pixel level using a triple layer thin film approach, where two films with different compositions contact a common electrode layer. Unfortunately, this does not provide an obvious path for continuous multiwavelength detection. To address this issue, we propose to utilize the unique properties of carbon nanotubes (CNTs) to demonstrate an infrared pixel with continuously and dynamically tunable absorption. The concept relies on the fact that the bandgap of CNTs is sensitive to strain, with a change of 100 meV per percent strain, as demonstrated experimentally and theoretically. By fabricating a CNT nanoelectromechanical (NEM) device, we will control the strain applied to the CNTs and achieve tunability of the optical absorption. Such CNT NEMS have been demonstrated with resonant frequencies of tens of MHz, and can thus be rapidly tuned. Our experimental work will be coupled with theory and modeling of the photophysics of strained CNT devices. Finally, we will test the radiation hardness (rad-hard) of these devices.

Summary of Accomplishments:
We extended our many-body ab initio calculations of the impact of strain on carbon nanotubes to a wider set of nanotubes and demonstrated that the approach is general. We also calculated the optical spectra and showed the tunability of the absorption peak with strain.

We developed two new approaches to fabricate suspended carbon nanotube devices that do not rely on chemical vapor deposition (CVD) growth across a trench. In the first case, we showed that nanoimprint lithography as a stamping method can produce good quality field-effect transistor (FET) devices. In the second approach, we fabricated suspended Schottky diodes using a novel “suspended beam” approach to achieve two-metal deposition.

We tested the Schottky diodes for optoelectronic response and discovered an unusual photocurrent response at reverse bias where the photocurrent increases with bias. This discovery will be explored in more detail in FY 2012.

We fabricated carbon nanotube FETs and tested them before and after proton irradiation with 10-MeV protons. We found that almost all devices survived, indicating that the single-tube devices could be inherently rad-hard.

Significance:
Infrared photodetectors play a key role across DOE mission areas being used, for example, in space-based surveillance for nonproliferation, thermal imaging for energy, and for stockpile stewardship. The proposed work with carbon nanotubes will allow the development of IR detectors with new functionality that will impact all of these areas. Because IR photodetectors are used in many science applications from the nanoscale to the cosmic, this work will also impact DOE's science mission.

Efficient, High-Voltage, High-Impedance GaN/AlGaN Power FET and Diode Switches
141517

Year 2 of 3
Principal Investigator: A. G. Baca

Project Purpose:
The purpose of this project is to understand whether lateral GaN transistors can make better, more promising solid-state, high-voltage devices. High-voltage, solid-state power conversion technology is a key enabler for increasing the penetration of renewable energy electricity sources through the ability to enable a wide variety of power conversion needs: high-voltage direct current (DC) transmission, DC/alternating current (AC), AC/DC, or DC/DC conversion for transmission or distribution. Conventional solid-state power conversion either operates at insufficient voltage levels or, as in light-triggered thyristors, is costly, lacks sufficient ruggedness and efficiency to be widely deployed. Conventional bulk drift devices (e.g., Si thyristor) are sufficiently mature, such that theoretical and practical limits to breakdown, based on the minimum controllable doping level, have not significantly changed in 30 years.

We propose to study and improve the lateral GaN/AlGaN transistor because its conductive properties arise from charge polarization effects without intentional doping and, therefore, may have a considerably higher breakdown limit. The goal is to achieve breakdown beyond 20 kV. Such a goal does not lend itself to an engineering solution because the wide variety of device structures and material combinations that must be fabricated and tested at high voltages is uneconomical. Rather, a science-based approach of studying and understanding the effects of device design and material combinations on leakage currents that limit breakdown at <5 kV (wafer probe limit) to build a model that scales beyond 20 kV is warranted. The main technical challenges include, among others, understanding the factors limiting breakdown field in these lateral devices, understanding the role of material/geometry/voltage on leakage, peak electric fields, and role of surface passivation. A science-based approach dictates that innovative solutions depend on which factors are found to limit breakdown. We have planned for novel controlled-ambient passivation (metal organic chemical vapor deposition [MOCVD]), SiN or AlN for surface leakage limiting, multiple field-plate electrode design (peak electric field limiting), and structural back confinement approaches (buffer leakage limiting).

Summary of Accomplishments:
We have made good progress in understanding the role of two factors that can limit breakdown voltage in GaN transistors. We explored the use of carbon doping in GaN buffers in order to prevent punch-through, an effect where the electric fields induced by a large drain-source bias will open up a conducting channel and act as though the device breakdown voltage has been exceeded. Technology computer-aided design (TCAD) simulations indicated that high carbon impurity levels in the GaN buffer was effective in preventing punch-through. Experimentally, we confirmed that carbon impurity levels near $10^{19}/cm^3$ were effective in preventing punch-through in GaN transistors.

We also explored the effect of placement and bias of standard and multiple field plate electrodes for GaN transistors and made good progress in understanding the scalability of electrode design so that the transistors can effectively reach much higher voltages. Using TCAD simulations, we compared the conventional gate layout with a field plate design and with a multi-electrode design. A multi-electrode design using a single applied voltage for all electrodes was shown to be a promising design for scaling to high voltage as the source-drain spacing is increased. This design effectively creates multiple peaks in the electric field versus gate-drain dimension, as opposed to merely increasing the separation between the electric field peaks versus gate-drain dimension in the standard field plate approach. The multi-electrode design holds promise for being scalable in a more predictable way than approaches that raise the average electric field through surface passivation techniques.

We also made improvements in the breakdown field in the transistors we fabricated in FY 2011. Transistors with a 4-micrometer gate-drain spacing achieved breakdown voltage of 400 V, for a breakdown field of 100 V per micrometer, which was approximately a three-fold improvement over FY 2010.

Significance:
Energy independence is a national security issue. As our nation develops alternative energy sources, a smarter and more efficient electric grid is needed to connect to distributed energy sources and to manage and balance the resulting loads efficiently and with robust security built into the system design. Sandia has a mission to assess and provide technology solutions for enabling and securing a future electric grid that meets these needs.

Electrodeposition of Scalable Nanostructured Thermoelectric Devices with High Efficiency
141518

Year 2 of 3
Principal Investigator: P. A. Sharma

Project Purpose:
The purpose of this project is to create nanostructured thermoelectric (TE) materials at bulk length scales using electrodeposition and solvent chemistry routes. While — according to the literature — nanostructured TE materials have been demonstrated using these methods, no attempts have been made at scaling these processes to millimeter dimensions or rigorously analyzing the structure-property relations in materials made these ways. This project focuses on both scaling and optimizing materials properties for use in the next generation of thermoelectric modules. Nanostructured thermoelectrics have been shown to have superior efficiency for both power generation and refrigeration applications, but their existing limited dimensions have prevented their real-world use in these areas.

This project directly addresses a technology that could revolutionize refrigeration and power generation. Present nanostructured TEs are not only limited in scale, but also have, as reported in the literature, irreproducible properties due to uncontrolled microstructure and carrier doping. Our project focuses on these two roadblocks simultaneously because if we succeed in fabricating a bulk scale nanostructured TE, we will then be able to systematically study how nanostructure affects transport using more reliable bulk measurements.

Summary of Accomplishments:
Optimization and Nanostructuring of Electrodeposits: Synthesized high-quality Sb_2Te_3 and Bi_2Te_3 deposits. Synthesized oriented, large area Bi_2Te_3/ Sb_2Te_3 superlattices. This chemistry was determined to be a good starting point for scale up. We submitted two papers to *Chemistry of Materials* and one paper to *Nanoletters* in these areas.

Transport and Microscopy of Nanostructured Deposits: Through extensive microscopy studies, we characterized deposits and nanostructured materials. We determined how to measure superlattice spacing and stoichiometry, and using this information, made adjustments in the plating process. Transport measurements proved difficult on the conducting substrates, so we found a better transport method that was insensitive to the substrate. We published a paper on the thermal transport in Bi_2-Bi_2Te_3 superlattices in *Physical Review B*, elaborating the particular source of defects that resulted in a reduced thermal conductivity.

Ab initio Calculations for Nanostructured Geometries: Compared generalized gradient approximations (GGA) versus local density approximation (LDA) within the ab initio density functional theory (DFT) approach in order to analyze electronic structure of superlattice intermetallics.

Transport Modeling of Nanostructured Deposits and Varying Nanostructure Properties of Deposits: We have determined a method for varying the superlattice periodicity and grain size of our nanomaterials through chemistry. Preliminary thermal conductivity measurements have been performed on superlattice samples. These results are still being interpreted.

Optimization and Scale-up of p-type Nanostructured Deposits: We purchased and set up an electroforming bath capable of yielding millimeter-size samples.

We have removed impurities from our deposits and nanomaterials and optimized the stoichiometry of our deposits and nanoparticles. Nanoparticle batches of more than 10 g have been synthesized and sent to Clemson University for consolidation. A large pellet of nanomaterials has been successfully made and awaits further transport measurements.

We have presented three different papers on the results of this work.

Significance:
TE devices are used for power generation and solid-state refrigeration applications, and impact such areas as vehicle electrification, increasing detector sensitivity through spot cooling, nondestructive testing, biometrics, night-vision, and remote power sources. This project aims to build the foundation for creating next generation TE devices and, therefore, is relevant to both national and energy security missions of DOE.

Refereed Communications:
P.A. Sharma, A.L. Lima Sharma, D.L. Medlin, A.M. Morales, N. Yang, M. Barney, J. He, F. Drymiotis, J. Turner, and T.M. Tritt, "Low Phonon Thermal Conductivity of Layered $(Bi_2)_m$-$(Bi_2Te_3)_n$ Thermoelectric Alloys," *Physical Review B*, vol. 83, p. 235209, June 2011.

J.R. Jeffries, A.L. Lima Sharma, P.A. Sharma, C.D. Spataru, S.K. McCall, J.D. Sugar, S.T. Weir, and Y.K. Vohra, "Distinct Superconducting States in the Pressure-Induced Metallic Structures of the Nominal Semimetal Bi_4Te_3," *Physical Review B*, vol. 84, p. 092505, September 2011.

Greater-Than-50% Efficient Photovoltaic Solar Cells
141519

Year 2 of 3
Principal Investigator: G. N. Nielson

Project Purpose:
We are developing a new photovoltaic (PV) cell structure that will allow solar power conversion of 50%. "Hero" monolithically grown laboratory cells have achieved approximately 42%. However, these cells have a number of constraints that limit efficiency, including lattice matched material requirements resulting in non-optimum bandgaps and inefficiencies in converting time-varying solar spectra from the series connected cells. To exceed 50% efficiency, we will integrate individually grown and connected junctions. This avoids degradation due to lattice mismatch, reduces series resistance losses, allows ideal bandgaps for maximum efficiency, and eliminates current matching so the cell stack can operate well in any solar spectrum. Key ST&E challenges include development of materials and cells for junctions of the proper bandgaps, the heterogeneous integration of cells, and developing micro-concentrators. The first prototype structure will be a three-junction cell of InGaAs, Si, and InGaP. Next, we will develop a four-junction cell comprised of InGaAs, Si or (Al)GaAs, InGaP, and InGaN. In parallel, we will also look at InGaN-GaN nanowire architectures that can absorb the entire solar spectrum.

To exceed 50% photovoltaic efficiency, we will create a stacked structure of individually grown and contacted cells, avoiding lattice and current matching requirements. We will first develop a three-junction cell comprised of InGaAs, Si, and InGaP. These junctions will be assembled within a receiver substrate and use concentrating optics for testing. Significant effort will be put into minimizing the optical losses in the cell stack. We will next develop a four-junction cell of InGaAs, Si or (Al)GaAs, InGaP, and InGaN resulting in efficiencies greater than 50%. The development of the InGaN junction will require developing new growth techniques to achieve the desired bandgap using strain-relief structures and nanowire architectures. Finally, graded-InGaN/GaN core-shell nanowire structures will be developed that absorb the entire solar spectrum in a single junction.

Summary of Accomplishments:
The materials and cell development efforts are on schedule or ahead of schedule. We have demonstrated key packaging elements required for the PV cell structure. We have designed, fabricated, and tested the microlens concentrator for testing the cells. We have demonstrated two-junction cells (GaAs and InGaP) and three-junction cells (Silicon, GaAs, and InGaP). We have also modeled the interconnection scheme to optimize performance from individual junctions.

Material development is progressing. We have created one-micron-thick, 21% indium composition InGaN grown on a porous GaN layer. We have created InGaN superlattice PV cells with 17% composition, and with a reduced bandgap due to the superlattice.

We are taking advantage of InGaAs photovoltaic cells developed at Sandia that provide high performance at 0.6 eV which allows us to eliminate the Ge cell development. The device structure and contacting scheme will need to be modified, but this allows significant risk reduction in the project.

We have demonstrated backside-contacted GaAs cells that are 11% efficient and are only 2.6 microns thick. We have also demonstrated back-contacted, dual junction GaAs/InGaP cells at 12.5%. We need to improve the efficiency, but this is a significant step forward.

We have demonstrated the ability to create plated indium bumps on aluminum for the packaging of the cells and have used these bumps to bond cells to a silicon substrate. This allows the multi-level packaging that the stacked cells require. With this technique, we have demonstrated a Si/GaAs/InGaP triple-junction cell.

We have designed and fabricated a microlens system that provides concentration of 49x and collimates the incoming light.

Finally, we have created a cell interconnect model that has given interesting preliminary behaviors; allowing optimized performance of the stacked cell structure, improved shading performance, and fault tolerance.

Significance:
This project explores new materials and microsystems concepts for solar power, utilizing Sandia's significant facilities and expertise in microsystems.

At the cell level, this project develops a new PV cell with the potential to exceed 50% efficiency. This would provide a much higher amount of output power per area than any previous PV technology. This revolutionary energy source would be most useful for reducing the size and weight of satellites and unmanned aerial vehicles, minimizing the area footprint of PV systems deployed for remote military operations, replacing hydrocarbon fuel supplies for electricity generation, shrinking the size of batteries needed for energy storage, and enabling significant balance-of-system cost reductions for solar power for the nation's electric grid — all key missions of DOE.

At the module level, this project utilizes microdesign, microfabrication, and semiconductor manufacturing techniques to produce modules comprising thousands of micro-PV cells. By using tools and techniques that have produced dramatic cost reductions in the semiconductor, liquid crystal displays (LCD), and light-emitting diode (LED) industry, this project can put PV technology on a path where solar PV can become the most convenient, most versatile, and lowest cost energy option for the end user.

At the system level, this project has produced designs for the microlens array and cell interconnection system that can reduce the overall derate factor of the concentrated PV system. This is important because state-of-the-art concentrator photovoltaic (CPV) systems with >40% efficiency PV cells tend to have derate factors of approximately 50%, resulting in CPV modules that perform no better than one-sun, c-Si modules. By systematically reducing the compounding losses in the optics, tracking system, and module circuitry, our MEPV concentrator design has the ability to produce electricity at potentially record-breaking photon-to-alternating current (AC) microsystems-enabled photovoltaic electricity efficiencies.

Overall, this project highlights Sandia's ability to contribute to US energy independence, opening up new avenues for solar funding and augmenting renewable energy (solar) efforts at Sandia.

The impact of the results from this project to date include the following: 1) a follow-on project to achieve world-record level PV cell performance (>50%); 2) the creation of a new microsystem-enabled PV paradigm; 3) new designs of an optical tracking approach for PV systems suitable for cheaper, coarse, single-axis tracking; 4) development of new methods of growing high indium content InGaN; 5) development of a 2.25-eV InGaN PV cell; 6) the publication of peer-reviewed technical articles in relevant conferences and journals; 7) development of significant intellectual property related to extreme high-efficiency PV.

Refereed Communications:

J.L. Cruz-Campa, M. Okandan, P.J. Resnick, P. Clews, T. Pluym, R.K. Grubbs, V.P. Gupta, D. Zubia, and G.N. Nielson, "Microsystem Enabled Photovoltaics: 14.9% Efficient 14 µm Thick Crystalline Silicon Solar Cell," *Solar Energy Materials and Solar Cells*, vol. 95, pp. 551-558, February 2011.

J.L. Cruz-Campa, G.N. Nielson, P.J. Resnick, C.A. Sánchez, P.J. Clews, M. Okandan, T. Friedmann, and V.P. Gupta, "Ultrathin Flexible Crystalline Silicon: Microsystems Enabled Photovoltaics," *IEEE Journal of Photovoltaics*, vol. 1, pp. 3-8, July 2011.

N.B. Crane, F. Tuckerman, and G.N. Nielson, "Self-Assembly in Additive Manufacturing: Opportunities and Obstacles," *Rapid Prototyping Journal*, vol. 17, pp. 211-217, March 2011.

G.N. Nielson, M. Okandan, J.L. Cruz-Campa, P.J. Resnick, M.W. Wanlass, P.J. Clews, T.C. Pluym, C.A. Sánchez, and V.P. Gupta, "Microfabrication of Microsystem-Enabled Photovoltaic (MEPV) Cells," SPIE Photonics West, San Francisco, CA, January 2011.

Microfabricated Nitrogen-Phosphorus Detector: Chemically Mediated Thermionic Emission
141520

Year 2 of 3
Principal Investigator: R. J. Simonson

Project Purpose:
In spite of the long history (~ 30 years) of Nitrogen-Phosphorus Detectors (NPD), the details of this chemically mediated emission phenomenon are currently not understood. While the N- and P-sensitivity of such devices for detection can exceed that for other hydrocarbons by 10,000x, the NPD signal current ultimately depends on the transfer of electrons across the surface potential barrier of the thermionic cathode (emitter). The transfer of charge carriers at high temperature is extremely complex at the nanoscale in these ceramic emitter materials. As military and homeland security needs drive requirements for smaller and more powerful detection technologies, operational problems, including limited source lifetime and high power consumption, become increasingly severe. This necessitates the development of a new micro-NPD. If successful, these devices will improve selectivity, speed, sensitivity, and portability of detectors for explosives, toxic industrial chemicals (TICs), and chemical warfare agents. Two classes of competing mechanisms have been described in the literature to account for the chemically selective ionization observed in NPDs: 1) gas-phase ionization models and 2) surface-mediated electron emission. The latter mechanism is considered more likely based on observations from the literature. In order to both investigate the proposed surface-mediated ionization mechanism and to improve performance of microfabricated NPDs, a systematic study of novel candidate thermionic emission materials will be conducted. Candidate materials include sol-gel deposited alkali-doped high-porosity silicate films, as well as mixed oxide films based on electron device cathode materials. Our approach will involve a multidisciplinary team to develop several unique NPD aspects, including direct measurement of surface variations in work-function of novel materials by scanning probe methods, systematic correlation of novel cathode material composition and microstructure with both work-function and NPD performance, and the design and test of novel microfabricated cathode structures for micro-NPD applications.

Summary of Accomplishments:
Our approach is based on the hypothesis that charge transfer between the thermionic emission cathode materials and the electronegative nitrogen- and phosphorus-containing organic molecules is a rate-determining step in the selective ionization mechanism. Accordingly, project goals and milestones seek to correlate ionization selectivity and sensitivity with the measured electron work function of candidate emitter film materials. To date, our team has accomplished the following:

1. Fabricated two types of low heat capacity micro-hotplate structures for use as micro-NPD substrates. These rely on doped Si resistive heater elements and encapsulated tungsten elements.
2. Synthesized novel alkoxide ligands and used them as solution precursors for deposition of high surface area thin film silicate thermionic emission cathodes.
3. Measured the work function of a range of doped silicates (Rb, Cs, Ca, and Ba-doped) using scanning Kelvin probe measurements.
4. Developed a direct thermionic electron emission measurement (TEEM) technique for measurement of thin film work function and emission current density at high temperatures (up to 650 °C).
5. Characterized the deposited thin films by x-ray photoemission spectroscopy, x-ray diffraction, and scanning electron microscopy.
6. Demonstrated selective ionization of organic vapors using prototype micro-NPD devices with doped silicate emitter cathode films. We have observed correlations between electron work function and the sensitivity and selectivity of ionization in these experiments. Ion current at fixed analyte

concentrations (sensitivity) increases as work function decreases, supporting the hypothesis that charge transfer is a rate-limiting step in the ionization reaction. Conversely, the selectivity of ionization of phosphonate compounds vs. saturated hydrocarbons decreases as work function decreases. In the future, we intend to explore the mechanism of ionization selectivity by widening the range of compounds tested and comparing their ionization selectivity with free electron impact ionization cross sections in the literature.

Significance:

Sandia is a leading developer of microscale chemical detection technologies for defense, homeland security, and intelligence agencies. Potential collaborators (Defense Threat Reduction Agency, intelligence agencies, DHS Chemical and Biological Defense branch) have expressed interest in fieldable nitrogen-phosphorus detector-based microsystems, but the presently available knowledge of selective emission/ionization materials is insufficient for successful device scaling. Success in this project can eventually enable new devices with the capability of meeting DoD and DHS chemical monitoring requirements.

Refereed Communications:

T.J. Boyle, L.A.M. Ottley, A. Saad, M.A. Rodriguez, T.M. Alam, and S.K. McIntyre, "Structural Characterization of a New Family of Cesium Aryloxides," to be published in *Inorganic Chemistry*.

Nanoporous Polymer Thin Films from Tri-Block Copolymers
141521

Year 2 of 3
Principal Investigator: J. G. Cordaro

Project Purpose:
This project combines our expertise in polymer synthesis, computational modeling, fabrication, and characterization of thin-films, and membrane testing, to create new nanoporous polymer membranes. Our goal is to design and make block copolymers that will self-assemble into thermodynamically favorable, ordered nanodomains suitable for chemical modification in order to control transport properties. Current membrane applications are limited by poor ion-selectivity, environmental conditions, difficult and expensive manufacturing techniques, ill-defined nanostructure, and weak mechanical properties. By controlling the morphology and pore selectivity on the nanoscale, many such limitations may possibly be overcome. Furthermore, by decoupling the mechanical and chemical components of the membrane, improved performance, including longer lifetimes, greater specificity, and altogether novel behavior from these new membranes will be realized. Robust thin-film polymer membranes with chemically tunable properties are the goal of this research.

Our approach is to make a triblock copolymer with a middle block segment that contains chemically reactive functional groups for post-annealing modification. We intend to develop new methods to selectively functionalize the nanoporous channels of this polymer thin-film and control permeability — an idea not described in the literature. While we will focus on a battery separator membrane and test its ion permeability, the approach is general because of the tunability of the membrane properties through chemical modification and polymer selection. Our “materials by design” approach will address the technical challenges associated with using polymer membranes in various applications. If successful, the proposed research will give us the tools and platform from which better membranes will be built. The results of this work will impact our efforts at Sandia to develop new energy storage devices and pave the way for expanding efforts into other DOE areas such as water purification systems, fuel cells, and bio-detection.

Summary of Accomplishments:
In FY 2011, we synthesized a di-functional initiator for the polymerization of methylacrylates and vinyl monomers using atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP). This initiator was reported in the literature but required some modifications to the experimental procedure to obtain material in large quantities and high purity. With this initiator, we synthesized a series of poly (methyl methacrylate) (PMMA)-macroinitiators with molecular weights ranging from 14,000–30,000 g/mol. Block polymers were also synthesized for these macroinitiators to give PMMA-b-PS (polystyrene). We learned that chain extension from a macroinitiator is much more difficult than anticipated. We also learned that ATRP techniques for polymerizing methacrylates require much more diligence than reported in the literature. Despite the steep learning curve, we were able to beginning working with the five diblock polymers to study microphase-separation.

In related work, we analyzed three polystyrene-b-poly(ethylene oxide) (PS-b-PEO) diblock polymers using small angle x-ray scattering and neutron scattering techniques. The goal of this work was to determine whether the PS-b-PEO material had phase-separated into a bicontinuous or disordered cylinder morphology. A phase-diagram for this material has not been published and our chosen molecular weights for the PS-b-PEO were based on FY 2010 calculations. What we learned was that annealing times and conditions for polymers containing long polystyrene (PS) segments require additional time compared to shorter PS-b-PMMA block polymers. Many other difficulties associated with PS-b-PEO block polymers were discovered. These challenges have led us to eliminate using PS-b-PEO as a potential template for ordered membranes.

Finally, we began a collaboration with University of California, Santa Barbara to extend our computational modeling work to include kinetic parameters.

Significance:

The proposed synergy of synthetic polymer chemistry, materials characterization, and self-consistent field theory (SCFT) calculations can lead to new and flexible methods for functionalizing ordered, nanostructured polymer membranes. Our work specifically addresses basic research efforts to understand materials properties across the "atomistic-to-micro-scale." This project is directly aligned with current projects in DOE and DHS, which emphasize energy storage and conversion, detectors, smart materials, and homeland security. A fundamental understanding regarding control and manipulation of nanoscale properties will be realized through this work. Success in this project will enhance Sandia's ability to respond to national needs in a variety of technical areas.

Surface Engineering of Electrospun Fibers to Optimize Ion and Electron Transport in Li^+ Battery Cathodes
141522

Year 2 of 3
Principal Investigator: N. S. Bell

Project Purpose:
The purpose of this project is to develop a materials processing strategy to enable the stabilization of a heretofore low cost but unstable cathode material, lithium manganese oxide spinel. The limiting component in lithium ion battery technology is the cathode material. Efficient cycling to produce power rapidly requires a small diffusion length for the Li^+ ion within the cathode structure and favors nanosized crystals. For the $LiMn_2O_4$ spinel structure, the cost of the material is low, but the oxide becomes unstable during cycling and dissolves, leading to capacity loss and low cycling stability. For nanopowder systems, a coating of a chemically inert oxide such as zirconia or alumina has been employed to stabilize the active material and extend the cycle life over hundreds or thousands of charge/discharge cycles. Electrical conductivity of the cathode formulation is also a significant factor in battery cycling, and is typically solved in a powder by the incorporation of conductive carbon black. Nanofibrous architecture of the cathode core material with a passivating shell of ceramic oxide is a solution to both issues of nanostructured active material as well as a potentially conductive network for the charge/discharge cycle. This project seeks to develop fabrication routes toward nanofibrous networks with a protective oxide coating, leading to the viability of a heretofore unsuitable cathode material. The project has applied techniques using sol-gel or other liquid-phase polymer solution precursors to the core $LiMn_2O_4$ material with a ZrO_2 shell coating to form fibrous networks, in situ characterization of the electrochemical behavior characteristics, bulk electrochemical cycling characterization, and theoretical treatment of the battery electrolyte stability to understand the stability of the core cathode material as well as the degradation process for the solid and the solvent.

Summary of Accomplishments:
We demonstrated the formation of fibrous networks of the core material ($LiMn_2O_4$) using two processes: electrospinning and forcespinning. Upon calcination, we form nanosized crystals of the spinel phase in a polycrystalline fibrous network, which demonstrates the expected cycling behavior of the bulk material. Forcespinning of a sol-gel composition to form zirconia fibers was also successful, and has been submitted for publication.

Core-shell forcespinning has been demonstrated, and will continue with process development to encapsulate the core in a thin, contiguous layer of the passivating ZrO_2 shell material. In situ electrochemical atomic force microscopy (AFM) and scanning tunnel microscopy (STM) studies of bare $LiMn_2O_4$ fibers deposited on Au substrates have shown that the fibers are stable in the EC:DMC:$LiPF_6$ electrolyte at the open circuit potential and during 10 potential cycles up to 4.3V. The current voltage characteristic clearly shows the expected Li ion transport peaks. However, without a protective shell, sustained polarization at high potentials promotes Mn dissolution and fiber instability, confirming the need for our proposed core-shell structure. This study shows the dissolution of the nanofiber under the discharge potential of the bulk material, and the formation of non-active precipitate crystals after dissolution.

In the theoretical treatment, DFT+U techniques were applied to treat the interface between the cathode material spinel $Li_{(x)}Mn_2O_4$ and ethylene carbonate (EC), a main component of commercial battery electrolytes. We found that decomposition of EC on the (100) surface at x=0 (no Li) is exothermic by

0.3 eV, both at zero Kelvin, by about 0.3 eV for both isolated EC and liquid EC droplet. EC is not oxidized in the process.

Significance:
Forcespinning technology offers the potential for rapid and continuous production of fibrous morphologies for sol-gel compositions. This capability can be extended to other useful materials at Sandia related to energetic, thermal, catalytic or structural applications. For energy storage, this fiber morphology leverages the diffusion distance advantages of nanomaterials with the safety and processability of long fibers. The process development offers the potential to utilize a readily abundant material (Mn) as the cathode element of a Li^+ ion battery, leading to efficient commercial application of a previously unsuitable material. Mn is also readily abundant, and would offer a solution to material source limitations as noted for the rare earth elements.

In this project, these are the first in situ electrochemical scanning probe microscopy measurements on electrospun fibers for Li ion battery cathodes and are expected to draw great interest in the battery community. Furthermore, the development of our in situ electrochemical AFM/STM capability will allow unique studies of surface layers formed on other materials of interest for Sandia's energy missions.

Sandia is nationally recognized as lead laboratory in electricity storage safety and reliability (S&R). A significant advance in the area of electrode-electrolyte interface stability and reaction control would strengthen this position and likely lead to interactions with other federal agencies. Our technique is inherently scalable for large format applications (e.g., hybrid vehicles stationary storage).

Understanding the High-Temperature Limit of THz Quantum Cascade Lasers (QCLs) Through Inverse Quantum Engineering (IQE)
141523

Year 2 of 3
Principal Investigator: I. Waldmueller

Project Purpose:
This project will answer the following question: "Is there a fundamental maximum operating temperature for Terahertz quantum cascade lasers (THz QCLs)?" The answer will have significant impact on determining what applications THz QCLs can address. Although the maximum operation temperature increased rapidly after THz QCLs were first invented in 2001, there has been very little improvement over the past few years and the maximum operation temperature achieved (185 K) still requires cryocooling. The slow progress has led many to speculate that the maximum operation temperature is fundamentally limited by the ratio of the photon energy to the thermal energy in the system ($h\nu/kT > 1$). While much data seems to fit this theory, recent results have significantly questioned the hypothesis and no good theories have yet replaced it. Many studies have explored how different design parameters affect laser performance, but with the existing techniques there has been limited direct connection between the studied parameters and the laser physics. This use of indirect measurements has resulted in a lack of systematic understanding. We propose to use the unique capabilities of our inverse-quantum-engineering (IQE) algorithm to systematically disentangle temperature-dependent, performance-limiting physics from the many interdependent material parameters of THz QCLs.

This project tries for the first time to design, test and compare "apples to apples" in order to systematically explore device physics. While, in principle, these structures could be designed by hand through significant trial and error, in practice it requires a computer generated design capability. Our algorithm is currently one-of-a-kind and can explore links between device performance and structure that could not be achieved before. This project is exploring the basic physics of devices with broad applicability rather than focusing on a particular application.

Summary of Accomplishments:
We used our IQE to design a set of frequency-shifted THz QCL lasers, i.e., a family of lasers with everything identical except for the lasing frequency. By growing, fabricating, and measuring the set of lasers, we obtained experimental proof that our IQE algorithm is capable of successfully frequency-shifting a given THz QCL design. Furthermore, the set of frequency-shifted lasers gave us unprecedented experimental access to a model system perfectly suited to isolate and directly investigate the impact of the laser frequency on laser performance. We showed that the maximum operation temperature depends more on the specifics of the design itself then the actual lasing frequency. This experimental result not only questions the belief that T_{max} is proportional to $h\nu$, but furthermore is a first important step in understanding the temperature dependence of THz QCLs.

With the goal to also investigate the temperature dependence theoretically, we developed a k-resolved, fully microscopic, quantum kinetic performance simulator which takes into account carrier-field interactions, carrier-phonon interactions, carrier-impurity interactions, carrier-carrier interactions including both diagonal and non-diagonal correlation contributions. Including numerically highly demanding features such as multi-subband screening, the non-equilibrium phonon distribution, and scattering to energetically higher subbands, we were able to achieve excellent agreement with in-house measurements. We showed that the developed simulator, which in contrast to previously existing simulators does not depend on any fit parameters, correctly predicts the current density for a wide range of lattice temperatures and applied voltages. First theoretical results on studies investigating the impact of the laser frequency on laser performance are consistent with our experimental results showing the importance of design specifications. The comprehensive data output of our simulator (heating, effectiveness of depletion mechanism, gain contributions) now allows us for the first time direct access to understand why one specific design is superior to another design.

Significance:

There are a growing number of laboratory demonstrations showing that terahertz (THz) frequency radiation can provide important solutions for on both DOE and DHS missions, such as screening applications (through package inspection, concealed weapon detection), component inspection, and molecular identification applications (explosive sensing at portals, and space-based remote sensing). A missing link for many applications is a compact, room temperature THz source. By improving our understanding of the physical mechanisms controlling operation temperature of THz QCLs, we should be able to improve the temperature performance.

Refereed Communications:

D.G. Allen, T. Hargett, J.L. Reno, A.A. Zinn, and M.C. Wanke, "Index Tuning for Precise Frequency Selection of Terahertz Quantum Cascade Lasers," *IEEE Photonics Technology Letters*, vol. 23, pp. 30-32, January 2011.

D.G. Allen, T.W. Hargett, J.L. Reno, W.W. Chow, and M.C. Wanke, "Optical Bistability from Domain Formation in Terahertz Quantum Cascade Lasers," *IEEE Journal of Selected Topics in Quantum Electronics*, vol. 17, pp. 222-228, January 2011.

Characterization of Failure Modes in Deep UV and Deep Green LEDs Utilizing Advanced Semiconductor Localization Techniques
147374

Year 2 of 3
Principal Investigator: M. A. Miller

Project Purpose:
In this project, we use innovative failure analysis (FA) techniques, particularly the Sandia-developed laser-based techniques, thermally induced voltage alteration (TIVA) and light-induced voltage alteration (LIVA) to study degradation mechanisms over the lifetime of optoelectronic devices emitting in the deep ultraviolet (270–280 nm) and the deep green (520–530 nm). The III-nitride material system has shown great success in light emitting devices from the deep ultraviolet (UV) to the deep green wavelengths. The nitride alloys of GaN, AlN and InN possess tunable direct bandgaps that have the potential to cover the entire visible spectrum and well into the UV. In order to broaden the commercial availability of III-nitride emitters, reliability, lifetimes, and efficiencies of optoelectronic devices emitting in the deep UV and green must be improved. Improvements at these wavelengths will have the greatest impact. A driving force for efficient long-lifetime green light emitting diodes (LEDs) is solid-state lighting, while applications for deep UV are in water and air purification, bioagent sensing, and optical communications.

Key to the efficiency and performance of these nitride-based LEDs as well as the continued expansion of available device wavelengths is the identification and fundamental insight into the failure modes of these devices. The target devices will be stressed at accelerated current densities to decrease time to failure. Identification of degradation mechanisms and subsequent corrective actions to reduce defects responsible for their degradation will lead to a potential screening method, improvements in optical efficiency, and increased lifetimes in III-nitride LED devices benefiting a host of applications from solid state lighting to bioagent detection.

Summary of Accomplishments:
TIVA and LIVA were successfully utilized to localize electrically active defects in both green and UV LEDs. Minimal deprocessing was necessary to image the commercially purchased devices. Before stressing the devices, we were able to characterize defect densities and defect signal behaviors as a function of both bias and wavelength. We demonstrated that the density or defect types had an effect on the individual device electrical characteristics.

We were able to detect and monitor subtle changes in the TIVA/LIVA defect signals under accelerated stress conditions while observing the LED performance degradation. For the UV LEDs, bright defect signals (increased power) not present at time-zero appeared under reverse bias conditions after stress. In the green LEDs, initially bright, power increasing defect spots developed dark halos with increasing stress time and new, dark, power decreasing defect spots were formed. Materials characterization of the new signals revealed significant defects within the p-type contact metallization layer that forms the bond between the GaN-based chip and an underlying Si substrate. These metallization defects were activated with stress since the TIVA/LIVA signals were only visible post-stress. Transmission electron microscopy (TEM) cross-sectional analysis revealed Sn bond metal penetration to the metal/semiconductor interface. The reacted layers likely have a different metal/semiconductor work function, potentially increasing a parasitic contact resistance, reducing internal reflectivity of the initial Ag-based contact, and reducing the lifetime of the devices. Characterization of UV LEDs is under way.

We have also developed a screening method for active defects. For example, an intensity-versus-voltage (I-V) curve measured from low voltages up through the turn-on voltage of the device is monitored for a change in slope just prior to the turn-on voltage on a UV LED. The presence of the slope increase is indicative of dark, electrically active defects in the UV LEDs.

Significance:
This work shows the potential to isolate individual and multiple defects that lead to premature degradation and failure mechanisms in green and UV LEDs. Subsequent processing modifications to reduce the density of the targeted defects, potentially leading to increased lifetime, increased efficiency, and a broader nitride-based spectrum of available device wavelengths may come from the results. The application of the results may impact a wide variety of applications including solid-state lighting (DOE), bio-sensing (DHS), water and air purification (DOE and DHS), polymer curing, and a number of medical applications.

Application of the UV-developed methodology to all GaN-based LEDs may provide a quick, economical way to screen out devices and understand the electrical nature of defects. The correlation between increased leakage current and defect presence indicates that these defects may also produce a reliability concern over long-term use. The screening method as well as the TIVA/LIVA failure analysis (FA) techniques to localize defects could be used to help future III-nitride R&D efforts.

The results may also be leveraged to encourage collaboration efforts with commercial partners to directly localize defects related to potential failure modes. Industrial manufacturers of related technologies have already expressed interest in the defect-localization techniques.

Photoelectronic Characterization of Heterointerfaces
147942

Year 2 of 3
Principal Investigator: M. T. Brumbach

Project Purpose:
In many devices, including solar cells, transistors, etc., the performance relies on the electronic band structure at the internal interfaces of the device. Photoelectron spectroscopy can be used to map the band structure through careful analyses of the layer-by-layer formation of an interface where ionization potential, core level positions, and work function are monitored. The electronic offset between two materials in a photovoltaic directly relate to the output voltage of the solar cell. Poorly matched band structures may have insufficient potential offsets to drive the device, may facilitate recombination, and/or may induce barriers for charge transfer. Interfaces of organic/inorganic materials are not well understood and research on interfacial energy alignment in these systems has been lacking. Large assumptions are prevalent including the fact that interfacial energy level alignments are commonly assumed from bulk properties, and the effects of ubiquitous contamination are neglected. The objective of this work is to perform robust characterization of the electronic structure at real hybrid interfaces by tailoring the interfacial region for photoelectron spectroscopy. Interfacial self-assembled monolayers (SAM) will be utilized to induce dipoles of various magnitudes at the interface. Additionally, SAMs of two molecules with varying dipolar characteristics will be mixed into spatially organized structures through microcontact printing to systematically vary the dipole magnitude. Control of the surface work function through use of an organized mixed SAM has not been attempted, although it has been shown that mixed dipolar species do lead to a concentration dependent ionization potential. Patterning the interface has been shown to have a significant influence on the behavior of thick polymer films. Spectra will be interpreted for continuous shifts versus spectral superposition as a function of the spatial mixing of SAMs. The role of unknown species will be inferred from the energy band diagram of a real hybrid interface by understanding the role of known species in known geometries.

Summary of Accomplishments:
Initial work focused on a range of conducting polymers and deposition conditions that were conducive to photoelectron spectroscopic analyses. Poly(3-hexylthiophene) (P3HT) and poly(ethylene dioxythiophene) (PEDOT) were selected for deposition via spin coating and interfacing with zinc oxide and indium tin oxide (ITO), respectively. A photoresist master was prepared with patterned areas of varying shapes and dimensions for microcontact printing of SAMs via a poly(dimethyl siloxane) (PDMS) replica. Shadow mask patterning of thiols on gold was also performed. Photoelectron spectroscopy of patterned thiols showed that the etching process altered the residual SAM material, but patterning could be performed resulting in a spectral shoulder in ultraviolet photoelectron spectroscopy (UPS). This has been a new insight on the spatial influence of SAMs on UPS spectra. Diazoniums were also electrochemically grafted to ITO with varying terminal functional groups. This work has shown that the terminal functional group directly influences the measured work function. New work has focused on the use of interdigitated electrode (IDE) arrays as substrates for SAMs and thin polymer films. The use of IDE substrates allows for a unique implementation of differential charging where the interface between a thin polymer film and the pair of electrodes gives a simultaneous measurement of the interface under two separate conditions. The opportunity for varying the potential on the electrodes also can influence the charging of the interfaced polymer, and/or SAMs on the electrodes. Recent results have shown that it may be possible to image IDE features that are below the resolution limit of the instrument due to a Moire effect. If such an effect has been observed, it would be a new result for photoelectron spectroscopic imaging.

Significance:
This research is germane to a broad range of activities relevant to DOE and National Security since a wide range of solid-state devices depends on the energy level alignment at internal interfaces. Several specific device types that could benefit from advances in understanding band alignments are sensors (defense and environment), photovoltaics (energy), laser emitting diodes (LEDs) (energy), transistors, and microelectronics (science). This work also provides basic science research for advancing our knowledge of important materials systems.

Ion-Photon Quantum Interface: Entanglement Engineering
148549

Year 2 of 3
Principal Investigator: D. L. Moehring

Project Purpose:
Distributed quantum information processing requires a reliable quantum memory and a faithful carrier of quantum information. Trapped ion quantum bits (qubits) are the leading realization for quantum information storage due in large part to their very long coherence times and well developed laser interaction techniques. Photonic qubits, on the other hand, are the natural choice for the transport of quantum information because they can quickly travel long distances with a minimum of decoherence. The capability to entangle photons with trapped ions in a technologically relevant and scalable fashion would be an important achievement. We leverage the active and successful development of microfabricated semiconductor ion traps at Sandia's Microsystems and Engineering Sciences Applications (MESA) facility, and integrate a micro-optical cavity. Compared to current efforts in academic settings combining macro-sized ion traps and optical components, a micro-device will result in the dramatically increased speed and fidelity of ion-trap based quantum-networking protocols. The combination of technical expertise and fabrication knowledge at Sandia is a unique strength. Indeed, integrating smaller components will directly allow for a stronger quantum coherent interface between a single trapped ion and a single photon. If successful, this technology could lead to new demonstrations of fundamental physics properties and would open new avenues for scalable quantum networking architectures.

Summary of Accomplishments:
A number of important steps have been taken to achieve timely experimental demonstrations of the milestones of this project. First, we completed the design and fabrication of a radio- frequency (RF)-optimized ion trap for our ion-photon cavity quantum electrodynamics (cQED) experiments. This trap was recently inserted into a newly built and tested ultrahigh vacuum (UHV) chamber for testing. Next, we have finished the theoretical design and experimental testing of the cavity mirrors for the quantum electrodynamics (QED) apparatus. The mirrors, as well as the custom-built mounting hardware, have demonstrated suitability for project metrics. Other experimental measurements include the demonstration of ion-shuttling over a dielectric (diffractive-optical-element lens) surface without change to successful voltage solutions, and the imaging of an ion from an aluminum trap surface allowing for an increase in fluorescence light collection.

Significance:
This project complements the current Intelligent Advanced Research Projects Activity (IARPA)-sponsored ion-trap quantum information effort by developing a foundation for quantum networking capabilities. This effort will also result in a new quantum information science and technology (QIST) capability for Sandia and will further the strategic objective of providing technologically relevant engineering solutions for QIST implementation.

Refereed Communications:
D.L. Moehring and B.B. Blinov, "Quantum Optics: Exploring Remote Entanglement," *Nature Photonics*, vol. 5, pp. 454-456, July 2011.

Polyoxometalate "Solutions" for Energy Storage
150774

Year 2 of 3
Principal Investigator: T. M. Anderson

Project Purpose:
Energy consumption is projected to significantly increase globally by mid-century, and this increased need will be partially met through the use of renewable energy sources. Due to the intermittent nature of these resources, compatible large-scale energy storage devices must likewise be developed. Redox flow batteries, a rechargeable system that uses redox states of various species for charge and discharge purposes, represent a promising approach, provided higher energy densities and lower-cost materials can be developed. The primary goal of this work is to produce new dissolved charge storage species that will yield higher energy density than current technologies by operating via multi-electron reduction-oxidation processes in non-aqueous media. Building on the extensive inorganic materials synthesis and characterization expertise at Sandia, we are utilizing metal-oxide clusters polyoxometalates (POMs) as new, dissolved charge storage species. We are applying a suite of analytical techniques to evaluate the stability of POMs in various battery electrolytes in order to gain an understanding of the structural and dynamic properties of these transformational complexes. Although mononuclear and infinite-array metal oxides are sometimes utilized as charge storage species, the use of nanometer size metal-oxide clusters in any energy storage application is unprecedented. This is due, in part, to the paucity of data on these systems in non-aqueous media. In addition, most of the fundamental electrochemical properties have never been examined under conditions appropriate to achieve high battery efficiency. The ultimate goal of the project is to incorporate non-aqueous POM analytes into a redox flow cell configuration in order to store charge. By focusing on non-aqueous chemistry, we have the opportunity to work with wider voltage windows while simultaneously decreasing temperature sensitivity and increasing cycle life (and therefore decreasing costs).

Summary of Accomplishments:
We have successfully identified three POMs that can reversibly store charge (a silico-vanado-tungstate, a diphospho-vanado-tungstate, and a ferro-zinc-tungstate) in non-aqueous solvents. The silico-vanado-tungstate and diphospho-vanado-tungstate complexes are able to store more than one electron per molecule and therefore offer improved energy density over existing technology. All of these compounds are sensitive to both the nature of the solvent as well as the supporting electrolyte. Specifically, polar protic solvents tend to facilitate the multi-electron processes whereas polar aprotic solvents tend to suppress them. In addition, ammonium halide supporting electrolytes tend to narrow the voltage window to the point that multi-electron reactions are not feasible, whereas lithium triflate gives a wider window and thus significantly more flexibility in establishing wide enough voltage windows that facilitate the multi-electron process. We have also completed a set of solubility/stability studies on these three prototype energy storage solutions and found they are an order of magnitude more stable than the acidic solutions we previously examined. The latter activity was facilitated by enhanced stability monitoring capabilities via phosphorus, silicon, and vanadium nuclear magnetic resonance spectroscopy (NMR). Kinetic profiles have been collected on the highly conductive silico-vanado-tungstate (600 mS/cm) and diphospho-vanado-tungstate (300 mS/cm) compounds in a half-cell configuration. Both of these compounds undergo a reversible two-electron redox at approximately 0.1 V relative to Ag/AgCl with complete charge/discharge occurring in less than one hour. Initial cycle testing indicates a high efficiency (99%) relative to other well-characterized flow battery chemistries. We have now synthesized a series of new POMs offering minor systematic variations of the silico-vanado-tungstate complex so that we can determine what properties are most important in determining charge and discharge state(s).

Specifically, we have now varied vanadium content (and thereby charge) and geometry (site specific position of vanadium in the cluster). Electrochemical testing of these complexes is currently under way.

Significance:

The primary accomplishment of this work to date has been the discovery of new energy storage materials capable of undergoing multi-electron charge/discharge processes by the systematic variation of charge density, molecular symmetry, and metal populations. The elucidation of more of the fundamental properties of metal-oxide clusters will inevitably lead to the successful preparation of advanced materials with potential applications ranging from catalysis and molecular magnetism to medicine as well as energy storage technology. This new base of scientific expertise and technical capabilities in the directed synthesis and characterization of energy storage materials will be disseminated through publications and conferences. We also anticipate that our results will be leveraged in the acquisition of funding for future flow battery projects, primarily through the Office of Electricity. This project focuses on the DOE's goal of creating a more flexible, more reliable, and higher capacity US energy infrastructure by applying advanced science and technology to develop new materials for energy storage applications. It will further support DOE's missions of promoting carbon neutral technologies, reducing petroleum imports, and incorporating intermittent renewable energy sources into our electrical grid. We anticipate our results will enable widespread incorporation of low-carbon sources into stationary power generation for future US energy security. In short, we will provide a new path to boosting the energy efficiency of flow batteries.

Elucidating the Role of Interfacial Materials Properties in Microfluidic Packages
150968

Year 2 of 3
Principal Investigator: T. L. Edwards

Project Purpose:
Microsensors for chemical and biological detection have seen relatively little field application because the small size and low cost of the microsensor are offset by the large size, high cost, and complexity of the balance of the sensing system — principally, the required external pumps and valves. Attempts to integrate these components into the sensor's microfluidic package have been limited by the lack of software design tools to simulate microfluidic device performance. Software simulation, in turn, is limited by our understanding of the materials properties at the interfaces of plastic laminate layers comprising the package. This project will address these shortcomings by: 1) designing experiments to extract the relevant mechanical, thermal, electrical, and chemical properties of plastic laminate interfaces; 2) developing a multiphysics model incorporating these parameters for plastic laminate microfluidic devices; and 3) demonstrating the model's capabilities by designing, fabricating, and testing a microfluidic pump.

A number of technologies have been employed to create microfluidic packages for microsensors, including silicon and glass micromachining, ceramic laminates, plastic injection molding, hot embossing, cast molding, and plastic laminates. Of these, plastic laminate packaging provides an attractive combination of low capital and material cost, rapid prototyping, and complex mechanical and fluidic structures. This technology employs a variety of thin polymer and metal films bonded by adhesives, solvents, thermal fusion, and ultrasonic welding. The properties of these interfaces — thermal and electrical conductivity, mechanical deformation, adhesion strength, and chemical resistance — vary from the bulk properties of the laminate films and depend on the laminate composition and joining method employed. These interface properties will be the focus of this project. We will develop the experimental techniques required to measure them, use this information to populate a multiphysics model describing plastic laminate behavior, and, as a proof of concept demonstration, apply this model to design an integrated micropump, a key component for high-performance microfluidic systems.

Summary of Accomplishments:

- Developed a process for joining plastic laminates using thermal, adhesive, solvent welding. Still working on details for novel method of low-stress epoxy interface to join plastic laminates.

- Developed test structure to evaluate energy released as laminates delaminate in controlled way. This delamination front propagation is recorded by video and will be used in the numerical model.

- Developed a model of the test structure using COMSOL™ modeling software. Still in the process of integrating the test structure results with the model.

Significance:
The lack of a fundamental understanding of materials issues has limited the ability to design integrated complex components such as valves for microfluidic packages. This project will develop the capability for integrated microfluidic packaging design that will enable a greater range of fieldable chemical and biological microsensor systems in support of National Institutes of Health (NIH), DoD, DHS, and DOE national security missions.

Refereed Communications:

P.R. Miller, S.D. Gittard, T.L. Edwards, D.M. Lopez, X. Xiao, D.R. Wheeler, N.A. Monteiro-Riviere, S.M. Brozik, R. Polsky, and R.J. Narayan, "Integrated Carbon Fiber Electrodes Within Hollow Polymer Microneedles for Transdermal Electrochemical Sensing," *Biomicrofluidics*, vol. 5, p. 013415, March 2011.

Fundamental Study of Metal/Oxide/Metal Memristor Physics and Device Optimization
151174

Year 2 of 2
Principal Investigator: M. Marinella

Project Purpose:
In 2008, Hewlett Packard (HP) Labs Fellow Stanley Williams discovered that a titanium dioxide (TiO_2) capacitor he created was behaving in a similar manner to the "missing circuit element" theoretically predicted 40 years earlier by Leon Chua. Since then, this resistor with a memory of the amount of electric charge passing through it, or memristor, has gained attention for its potential advancement of applications such as neural networks. For example, by functioning as a synapse the memristor could enable complex learning and brain-like functionality in computers. However, before these applications can be realized, we must develop an understanding of memristor device physics and derive a detailed, predictive model of this device. While a basic analytical model has been suggested by HP, the physics of the metal/oxide/metal (MOM) memristor have not been rigorously investigated. Thus we have a major scientific challenge: to develop an understanding of memristor physics that is robust enough for us to predict the behavior of this complex device.

The physics of the TiO_2-based memristor is not well understood. HP Laboratories has suggested a basic mechanism but it has not yet been fully accepted by the scientific community. Furthermore, their patent has limited HP's scientific efforts to the TiO_2/platinum memristor, which is only one possible material system. A generalized physical model of the MOM memristor is the first step toward integrating it into new applications. Therefore, we propose to perform a fundamental study of the physics of resistive switching in MOM structures. This study will consist of three parts:
1. theoretical analysis of physical theories describing memristive behavior,
2. the fabrication of basic MOM memristors and characterization of these devices, and
3. the development of analytical models that reflects understanding of the physical properties of the memristor gained from (2), and that can be used to predict and simulate memristor behavior.

Summary of Accomplishments:
The most important accomplishment of this project was the successful development of the capability to fabricate and electrically characterize memristors using the Microsystems and Engineering Sciences Applications (MESA) facilities. This included establishing the necessary process in MESA, as well as creating advanced electrical characterization test protocols and analyses, such as hysteresis and pulsed current-voltage testing. Sandia is now considered a major government resource in the science, technology, and application of memristors. The cooperative research and development agreement (CRADA) with HP that resulted from this work has given us further legitimacy in this field. Through interactions with HP Labs, we have noted a number of electrical properties of the memristor that may be applicable to Sandia's National Security Mission. For example, early radiation testing has identified memristors as a candidate for an advanced rad-hard nonvolatile memory.

Another major accomplishment was the invention of a new type of memristor. Specific information is not detailed here due to patent issues, but it is based on a new material and a new class of materials that have not previously been proposed for use as a memory element. Memristors based on this new material have demonstrated a high on/off ratio which is useful for analog applications. The first lot of memristors with this material yielded devices with and endurance of over 100 cycles (one with 150 cycles). This is very promising for a first run, and surpasses the behavior of our original lots based on traditional materials like titanium dioxide.

Significance:
With interest arising in the areas of national security, nuclear weapons, high performance computing, and even neuromorphic systems, memristors appear to be one of the most crosscutting new technologies at Sandia. Memristors appear to represent a major candidate for a future radiation hard nonvolatile memory, which could be integrated on the back end with our current rad-hard complementary metal oxide semiconductor (CMOS) process. Furthermore, memristors can be programmed fast enough that they may play a role as a possible energy saving dynamic random access memory (DRAM) replacement in exascale supercomputers. External agencies are already funding further work to demonstrate the applicability of memristors to Sandia's mission areas.

Nanoscale Mechanisms in Advanced Aging of Materials during Storage of Spent "High Burnup" Nuclear Fuel
151328

Year 1 of 3
Principal Investigator: B. Clark

Project Purpose:
The purpose of this project is to understand the degradation of Zr-based cladding materials within the complex environment experienced during dry storage. This work was motivated by the decision to not pursue Yucca Mountain as a nuclear waste repository. The current policy of the Nuclear Regulatory Commission implies that spent nuclear fuel (SNF) will have to be stored in a retrievable condition for an indeterminate amount of time, conceivably on the order of centuries. Compounding this issue is the trend to discharge nuclear fuel after "high burnup," i.e., > 45 gigawatt-days per metric ton of uranium (GWd/MTU). Although the US has 24 years experience in storage of low burnup fuel, there is no precedent for storage of high burnup fuel, which produces more fission products leading to increasingly complex degradation mechanisms. Current efforts to model the degradation of materials during interim storage rely heavily on empirical equations, limiting their capacity for long time scale extrapolation. To provide fidelity in the ability to retrieve used fuel from storage either for transportation or further processing, extrapolative, physics-based models must be developed, and thus it becomes important to understand the degradation of materials within the complex environment experienced during storage. The details of these nanoscale degradation mechanisms will be pursued using high-resolution, gas-phase in situ transmission electron microscope (TEM) experiments coupled with mesoscale modeling.

Summary of Accomplishments:
We developed a technique to charge Zr-based cladding alloys with hydrogen in an aqueous solution. This was done to form a hydride on the cladding surface in a way that simulates the formation of hydride inside a nuclear reactor. Samples charged for various durations, and thus with different levels of hydriding, were analyzed via elastic recoil detection (ERD) to see the profile of hydrogen present in the cladding as a function of depth from the surface. The ERD data requires specialized analysis in order to get an accurate composition profile, but once successful, will provide new knowledge of the diffusion of hydrogen and formation of hydrides in Zr-based alloys at non-elevated temperatures. In addition, we have successfully developed a collaboration with Idaho National Laboratory to prepare and analyze actual spent fuel claddings. This analysis will be crucial for understanding the true microstructural changes that occur in service, enabling us to create simulated end-of-service microstructures for subsequent accelerated aging testing. Finally, we have made significant progress in preparing for in situ TEM gas cell experiments. Cladding material for three commercial alloys was obtained and prepared for TEM analysis of the starting microstructures. Also, the new in situ gas cell stage was received and we have begun to learn its use for future experiments, including developing a gas manifold system for introduction of custom gas mixtures into the stage and developing a method for introduction of cladding samples into the limited geometry of the stage.

Significance:
The results to date are providing new knowledge and details of the degradation in cladding materials both in service and in dry storage. Research into processes such as formation of hydrides, hydride reorientation, use of ions to simulate neutron damage, and the effect of irradiation defects on the uptake of hydrogen will directly impact efforts at Sandia to develop advanced storage solutions for nuclear waste. The successful completion of the proposed work could attract long-term, follow-on funding. In addition, the successful development of gas-phase in situ TEM capabilities for the study of complex,

elevated temperature and environmental gas environments could be extended for nanoscale investigations relevant to nuclear weapons surety, of significant importance to Sandia's mission.

Active Infrared Plasmonics
151329

Year 1 of 3
Principal Investigator: E. A. Shaner

Project Purpose:
The mid-infrared ([mid-IR], 3–12 microns) is a highly desirable spectral range for imaging, environmental sensing, and countermeasures. We propose to develop a new class of mid-IR devices, based on plasmonic and metamaterial concepts that are dynamically controlled by tunable semiconductor plasma resonances. It is well known that any material resonance (phonons, excitons, electron plasma) impacts dielectric properties; our primary challenge is to implement the tuning of a semiconductor plasma resonance with a voltage bias. We have demonstrated passive tuning of both plasmonic and metamaterial structures in the mid-IR using semiconductors plasmas. In the mid-IR, semiconductor carrier densities on the order of 5 x $10^{17}cm^{-3}$ to 2 x $10^{18}cm^{-3}$ are desirable for tuning effects. Gate control of carrier densities at the high end of this range is at or near the limit of what has been demonstrated in literature for transistor style devices. Combined with the fact that we are exploiting the optical properties of the device layers, rather than electrical, we are entering into interesting territory that has not been significantly explored to date.

The primary reason for this work is that the voltage control of resonances has been identified as high risk. Even though we have demonstrated passive mid-IR control of both plasmonic and metamaterial structures using semiconductor plasmas (by varying the density in doped epi-layers of GaAs and InSb), the dynamic tuning is the key effect needed for this research to progress. Once that capability has been demonstrated, electromagnetic simulations of plasmonic- and metamaterial-based beam-steering elements, reflectance modulators, filters, and emission control structures should reliably guide development efforts based on the known behavior of semiconductor device layers. While all of these potential applications have mechanical alternatives, it is well known that achieving similar functionality in non-mechanical solutions is desirable in terms of reduced size, weight, power requirements, and response times.

Summary of Accomplishments:
Our primary accomplishment was the demonstration of electronic plasmon resonance tuning using free carriers in GaAs and a Hafnia gate dielectric, resulting in two publications. The first publication tested the limits of free carrier tuning in GaAs-based single-sided plasmonic structures. The results of that work have led us to direct more focus onto metal-insulator-metal waveguide structures for phase shifting in order to acquire more phase shift with lower doping levels. We will also be focusing more strongly on coupling intersubband transitions to surface plasmons for both phase shifting and modulation.

Significance:
Plasmonic-based infrared beam steering would greatly benefit countermeasure applications and bolster DOE scientific discovery. The need for infrared sensing of biological and chemical materials has also been raised in importance in protecting our nation under the DHS strategic plan. Here, plasmonic devices may play a role in reaching new levels of sensitivity or improved detection schemes (for example, on-chip scanning infrared interferometers for sensing could be realized).

Refereed Communications:

K. Anglin, T. Ribaudo, D.C. Adams, X. Qian, W.D. Goodhue, S. Dooley, E.A. Shaner, and D. Wasserman, "Voltage-Controlled Active Mid-Infrared Plasmonic Devices," *Journal of Applied Physics*, vol. 109, p. 123103, June 2011.

J.C. Ginn, R.L. Jarecki, Jr., E.A. Shaner, and P.S. Davids, "Infrared Plasmons on Heavily-Doped Silicon," *Journal of Applied Physics*, vol. 110, p. 043110, August 2011.

Monolithically Integrated Coherent Mid-Infrared Receiver
151332

Year 1 of 3
Principal Investigator: M. Wanke

Project Purpose:
We propose to develop a coherent mid-infrared (MIR) receiver with the goal of achieving mid-infrared detectivity 100 times better than state-of-the-art room temperature MIR photodetectors. Conventional MIR photodetectors suffer from excess dark current due to thermal excitation of carriers at room temperature. Our goal is to use the nonlinear electrical response of a Schottky diode detector instead of the linear optical absorption response in photodetectors, and therefore eliminate dark current issues. Schottky detectors are commonly used at lower frequencies where they are integrated with antennas to couple light to the small diode. Although extremely sensitive at low frequencies, their sensitivity at higher frequencies has been limited due to the device capacitance, which shunts higher frequency signals from the antenna around the diode. We recently demonstrated an antenna-less method of coupling terahertz (THz) radiation to a Schottky diode, by inserting a diode active region directly into a laser core and using the surface plasmon to couple radiation into the diode. In this project, we will explore whether this new coupling geometry reduces the capacitive shunting and can enable highly sensitive integrated coherent mid-infrared detectors.

There are many uncertainties in this work: Does the new geometry eliminate the capacitance issue? Will the required surface plasmon coupling significantly impact the laser performance? Can planar Schottky diodes operate above a few THz? Can the mixer radio frequency (RF) response be coupled out with this geometry? While a Schottky diode heterodyne mixer could have significant application impact, this initial demonstration is focused on understanding these basic questions, research that is relatively immature and of high risk.

Summary of Accomplishments:
We designed MIR GaAs quantum cascade lasers (QCLs) based on InGaAs QCLs designed at Princeton University. GaAs was chosen so we could use the Schottky technology we previously applied in the THz. Our collaborators designed new waveguide cladding layers for the lasers so that the waveguide loss would not exceed the gain in the material while still allowing some to couple to the top metal where our diode would be placed. We have grown and fabricated these initial lasers. Unfortunately, the first growth attempt had problems and the lasers did not lase. The second growth run looks much better and the samples have been processed and recently mounted. Testing has just started.

While waiting for better MIR QCL growth, we continued exploring the physics of the diode behavior using previously fabricated THz transceivers. We measured the rectified response carefully to look at the behavior of the diode response. A typical Schottky diode is proportional to the curvature of the DC-IV (DC current-voltage curve). We only sometimes observe this behavior, while at other times, we observed behavior that was more similar (although not identical) to what we have observed in THz plasmon detectors. We have shared this data with a theorist at Kingsborough College who has done extensive modeling on plasmon-based 2D electron gas detectors; we are collaborating to build a new model. We designed and implemented a new measurement system to improve the measurement accuracy of the diode response as a function of laser power and diode current and are actively exploring the diode response in more detail.

Significance:

This project directly addresses DOE's scientific discovery and innovation thrust by exploring novel device integration and developing sensor technology that can be applied to environmental and security challenges. Our collaborators are working on remote chemical sensing testbeds and have multiple corporate partners, providing avenues for strategic partnerships between academia, industry and Sandia, which might ultimately move the developed technology out of the lab to solve national problems, such as detecting proliferation of nuclear material.

Non-Abelian Fractional Quantum Hall Effect for Fault-Resistant Topological Quantum Computation
151333

Year 1 of 3
Principal Investigator: W. Pan

Project Purpose:
The most secure modern encryption method is based on the assumption that it is impossible to prime-factorize a large digit number within a reasonable time frame. Indeed, it is estimated that factorizing a 200-digit number would require 170 CPU years using an Intel computer. This estimate, however, is drastically changed with the use of a quantum computer. In a paper published in 1994 by Peter Shor, he showed that a quantum computer (QC) could readily factorize a 300-digit number. This began a worldwide race to construct a QC. Yet, after 15 years of research, many fundamental issues remain unresolved. For example, the strong coupling between electrons and their local environments greatly reduces electron coherence time and requires complex error-correction schemes to manipulate quantum information before it is lost. As such, there is a pressing need to identify new paradigms that can potentially enable revolutionary advances in the field of quantum computation.

Topological quantum computation (TQC) has emerged as one of the most promising approaches. Under this approach, the topological properties of a non-Abelian quantum system, which are insensitive to local perturbations, are utilized to process and transport quantum information. The encoded information can be protected and rendered immune from nearly all environmental decoherence processes without additional error-correction. It is now generally believed that the low energy excitations of the so-called n=5/2 fractional quantum Hall (FQH) state may obey non-Abelian statistics. Our goal is to explore this novel FQH state and to understand and create a scientific foundation for exploiting this quantum matter state in order to build a knowledge base for the emerging TQC technology. We expect that success in this project would have a great impact on the feasibility of eventually building a topological computer.

Summary of Accomplishments:
We measured the activation energy gap of the 5/2 fractional quantum Hall state in two types of samples: symmetrically doped modulation quantum-well samples and undoped heterojunction insulated gate field-effect transistors (HIGFETs). In modulation-doped quantum-well samples, where long-range Coulombic disorder dominates, the energy gap drops quickly with decreasing mobility (or increasing disorder). On the other hand, in HIGFET samples, where the short-range neutral disorder dominates, the 5/2 energy gap shows only a weak mobility dependence. Our results clearly demonstrate that the two types of disorder play very different roles in affecting the stability of the 5/2 state. This result helps us to understand the impact of disorder on this fractional quantum Hall effect (FQHE) and to design an optimal device structure to obtain the largest energy gap at 5/2 and, thus, the lowest error rates in the envisioned topological quantum computation.

We designed photomask and successfully fabricated quantum point contact (QPC) devices using the conventional photolithography technique. By so doing, we were able to maintain high quality in the device. Using these QPC devices, we explored the non-Abelian physics of the 5/2 state. In detail, tunneling measurements were carried out as a function of Landau level filling and sample temperature. From these data, a quasi-particle charge of ~ e/4 was deduced for the 5/2 state. This value is in good agreement with theories. Our results thus strongly support the 5/2 state being a non-Abelian state.

Significance:
The proposed research adds to our strong and growing quantum information processing (QIP) research effort in an area where we have an exceptionally strong leadership position in the physics behind the proposed architecture. It is expected to lead to a possible demonstration of non-Abelian statistic properties or even a single qubit, which will eventually enable us to implement robust TQC. This investment will help to maintain our leadership and should position Sandia for significant follow-on funding opportunities.

Our FY 2011 results show that the conventional photolithography technique is capable of fabricating nanostructures for studying the non-Abelian physics of the 5/2 state while maintaining device quality. This may open a new avenue for future topological quantum computation applications.

Refereed Communications:
W. Pan, N. Masuhara, N.S. Sullivan, K.W. Baldwin, K.W. West, L.N. Pfeiffer, and D.C. Tsui, "Impact of Disorder on the 5/2 Fractional Quantum Hall State," *Physical Review Letters*, vol. 106, p. 206806, May 2011.

Germanium on Silicon Optoelectronics
151334

Year 1 of 3
Principal Investigator: P. Davids

Project Purpose:
Moore's law scaling of microprocessor technology development dictates that, within the next 10 years, power consumption in large-scale computers will be dominated by their electrical interconnects. One technology that has emerged as a potential solution to this bottleneck is silicon photonics. Yet, any optical interconnect is incomplete without a light source; owing to its indirect band gap, creating a homogeneously integrated optical source on a silicon platform has been the single most scientifically challenging problem in the field since its inception more than two decades ago. While heterogeneous wafer bonding of III-V laser sources to silicon photonic circuits has been demonstrated, this solution is ultimately undesirable due to both incompatibility with state-of-the-art silicon fabrication and yield issues. Recently, an optically pumped strained germanium on silicon laser was reported. This preliminary result indicates that with rigorous scientific analysis, an efficient electrically pumped laser source emitting in the technologically relevant communications wavelength band may be possible. Germanium does not suffer from the same incompatibility with the complementary metal oxide semiconductor (CMOS) process as do heterogeneous integration technologies. Further, germanium offers the ability to directly integrate a germanium receiver on a silicon platform, which enables direct integration with CMOS electronics reducing electrical parasitics and enabling high-speed, low-noise, and low-power receivers. The combination of these two scientific achievements would enable complete low-power photonic networks homogeneously integrated in silicon.

Development of an electrically pumped laser emitting at relevant optical communications wavelengths in a group IV semiconductor has never previously been achieved. Only through rigorous analysis of the band-structure, strain, doping concentration, and growth conditions will a successful demonstration be possible. Demonstration of an electrically pumped germanium-on-silicon laser would be a significant scientific and technological breakthrough in the field of silicon photonics, an enabling accomplishment for the future of the silicon photonics platform.

Summary of Accomplishments:
We have demonstrated a high-speed, ultracompact integrated waveguide Ge on Si photodetector. This detector has a measured 3-dB cutoff at 45 Ghz with less than 10 nA of dark current, with high responsivity (0.8 A/W) making it best in class. Our device is ultracompact, at 1.3 microns wide and 4 microns long, and it is the smallest 40 Gb/s integrated on-chip detector in Si photonics. This device is an essential building block for all integrated high-speed Si photonics receivers and is a significant milestone.

Furthermore, we have fabricated and tested the first lateral Ge on Si PIN photodetectors. Modification to these device designs is expected to yield electroluminescence diodes and form the basis for electrically injected Ge on Si amplifiers and lasers.

In order to characterize the optical properties, we have developed a flexible spectrometer setup to evaluate the optical properties of Ge. A pump laser diode is used to optically excite the Ge sample and a top-collect or side-collect configuration is routed to our spectrometer for analysis. This flexible setup allows for gain measurements in disk laser structures by examining whispering gallery modes and provides a more sensitive measure of gain. In addition to our optical setup, we have utilized x-ray diffraction to infer the strain in selectively grown Ge samples, and can then perform secondary ion mass spectrometry (SIMS) or spreading resistance profiling (SRP) to determine dopant profiles and completely characterize the samples.

Finally, we have developed a tight-binding bandstructure calculation to compute the optical absorption in strained and doped Ge. These parametrized electronic structure models have been used to compute the transport properties in advanced CMOS devices, however, we have adapted them to examine optical effect, such as free-carrier absorption. From our electronic structure models and measured parameters, we have also developed detailed material gain models.

Significance:
A complete silicon photonics platform that is CMOS compatible represents a new capability that will potentially have significant benefits across many DOE and DoD mission areas. From high-speed, low-power communications in high performance and embedded computers to radar, satellite and wireless communications applications, a complete silicon photonics platform will prove to have wide-ranging impact. The application impact extends across the DOE spectrum from Scientific Discovery and Innovation to Nuclear Security and American Competitiveness.

Refereed Communications:
C.T. DeRose, D.C. Trotter, W.A. Zortman, A.L. Starbuck, P.S. Davids, M. Fisher, and M.R. Watts, "Ultra Compact 45 GHz CMOS Compatible Germanium Waveguide Photodiode with Low Dark Current," to be published in *Optics Express*.

Fundamental Investigation of Chip-Scale Vacuum Micropumping (CSVMP) 151335

Year 1 of 3
Principal Investigator: R. P. Manginell

Project Purpose:
If important microtechnology like micro-mass-spectrometers or miniature atomic clocks are to be fielded, a chip-scale vacuum micropump (CSVMP) must be developed. Neither device can function for long in the field without a CSVMP. Yet, despite ~20 years of Defense Advanced Research Projects Agency (DARPA) funding, a truly useful CSVMP remains unrealized. The best designs generate 21 kPa (3 PSI) below atmospheric pressure and 5 cm^3/min flow. Are technological barriers to blame, or more fundamental issues? This project will take a focused approach to answering this question. Creating a vacuum micropump is undoubtedly challenging given the lack of lubricated seals on this scale and low relative dimensional/assembly tolerances. Importantly, the micropump literature does not consider free molecular flow (FMF) leaks, though FMF would be reached at only 0.03 kPa absolute in a working micropump. FMF backflow through nanoscale roughness in micropump seals can be $2x10^{-10}$ cm^3/sec, comparable to or exceeding the leak rates of vacuum packages they would ideally evacuate. FMF leaks could indeed fundamentally limit CSVMPs.

The foundational question posed in this project is novel: Is a gas micropump an impossibility or just a technical headache? This project will, for the first time, create an experimental platform for measuring micropump leaks. FMF measurements at these flows ($<10^{-10}$ kg/s) is extremely challenging; a handful of papers discuss the topic. Modeling/simulation will be performed and compared with experiment, providing the first micropump-relevant validated models. Theoretical understanding of transition and slip flows on these scales is nascent, and this research will contribute significantly to the field. The best method of modeling/simulation from transition to FMF is Direct Simulation Monte Carlo (DSMC), which requires massively parallel processing such as that available at Sandia. Validated models will be used to draw conclusions regarding fundamental CSVMP operation and to determine parameters for a functioning CSVMP.

Summary of Accomplishments:
To evaluate our vacuum/flow system, we added a goal this year, namely, to model/simulate rectangular-duct microchannels and compare against benchmark data. Validated models were used to predict the best rectangular-microchannel dimensions. We felt it important to test the experiment/theory against well-characterized flows in microducts before proceeding to lower flows and higher Knudsen numbers expected in micropumps. Analytical/numerical techniques DSMC were successfully used to meet our goal of modeling/simulation of benchmark data on the rectangular and circular microchannels. DSMC was particularly valuable in the transition regime. From this, we developed a matrix of rectangular microchannels that allow linearization of the kinetic flow equations and ensure that lateral-wall and end effects can be neglected over the experimental conditions.

We must hermetically mate a silicon lid to the etched silicon microchannels to maintain the same roughness and chemical makeup of the microchannel roof and floor. For this purpose, we advanced the state-of-the-art of plasma-assisted bonding (PAB). Wafer flatness and surface roughness were problems that were solved to drastically improve bonding yield and hermeticity. Acoustic microscopy assessed PAB yield, while He-leak checking verified hermeticity. He-leak checking was used to identify suitable adapters to connect the microchannels to the vacuum system. The vacuum system developed will allow measurement of flows ~1000 times lower and 2–4 times the Knudsen number of previously published work, from continuum to free molecular flow. This is a key, completed goal. We are validating our apparatus against benchmark data on our rectangular and circular microducts, in accordance with our milestones. We are developing methods necessary for creating a pump membrane that is hermetically sealed at its edges, but free in its central, active region, with a minimal gap in the active zone. This entails chemical-mechanical polishing an inert silicon nitride island in the active area, surrounded by a silicon-bonding perimeter.

Significance:
This project will contribute fundamentally to the understanding of rarefied gas flows, particularly in micropumps. Truly useful micropumps, with high flow, high pressure/vacuum and low power, have been elusive, despite years of research. Experimental and theoretical understanding of leaks in the nano-micro domains is lacking. The boundaries of measurement techniques and relevant theory must be extended to cover this technologically important flow regime. This project will operate with flows three orders of magnitude lower than previous work, and Knudsen numbers 2–4 times greater. This information is needed to truly understand leaks and flows in micropumps. Such novel experiments and validated modeling will shed new light on micropump fundamentals. The validated models will then be used to make predictions concerning micropump design. Engineered pump membrane texture and moving boundary DSMC will also be tested for the first time in this project in a micropump-relevant context.

This project is investigating the fundamentals of fluid flow in the nano-micro regime and will create the first relevant, validated models of such flows. This project will lay the groundwork for further funding in vacuum micropumps, several agencies having expressed interest in this research (DARPA, the Jet Propulsion Laboratory [JPL], and the National Aeronautics and Space Administration [NASA]). Without a CSVMP many investments like microelectromechanical system (MEMS) resonators/oscillators, micro-mass spectrometers, quantum computing, vacuum microelectronics and chemical sensors might not be useful in the field for extended periods of time. The fundamental science and modeling/simulation herein impacts many other fields, including vacuum microelectronics, rarefied gas flows, and microplasma research. To disseminate the knowledge gained in this work to the broader scientific community, several publications are planned.

Coherent Phonon Generation Through Nanoscale Enhanced Light-Matter Interaction: Towards Novel Silicon Lasers, Broadband Phononic Signal Processing and Optically Powered Micromechanics
151336

Year 1 of 3
Principal Investigator: P. T. Rakich

Project Purpose:
Through deeper understanding of the physics of nanoscale light-matter interactions (or nano-optomechanics), efficient light-driven coherent phonon generation could be exploited to realize significant performance improvements in radio-frequency (RF), phononic, acousto-optic and optical signal processing, and sensing technologies from a new class of hybrid photonic/phononic and photonic/microelectromechanical system (MEMS) devices. Development of efficient photon-phonon coupling mechanisms would yield enhancements in accelerometer/gyro technologies (10x–100x sensitivity), and optical/RF signal processing performance, arising from inherent advantages of phononic-domain signal processing. While the field of nano-optomechanics is rapidly progressing since its advent (~2007), the growth of high-impact technologies from this field will require, 1) new theories for treatment of nanoscale light-matter interactions, 2) the development of multiphysics models coupling photonic and phononic effects, and 3) new methods for fabrication and measurement of nano-optomechanical systems. Through an aggressive theoretical and experimental project investigating nanoscale light-matter interactions and enhancement mechanisms for photon-phonon coupling, we will advance the field of nano-optomechanics in these areas.

Enhancement of photon-phonon interactions, necessary to realize hybrid photonic/phononic technologies, requires improved understanding of the way mechanical motion is produced by light-induced forces at nanometer scales, and the physical mechanisms by which optical forces can be scaled to large values. We, and others, have recently shown that nanoscale light confinement can yield tremendous optical forces from radiation pressure, which are necessary to enhance photon-phonon interactions. Surprisingly, however, the lesser understood and widely ignored electrostrictive forces can also scale to tremendous values providing a significant new material-dependent means of enhancing and tailoring efficient light-driven coherent phonon generation. Through a recent theoretical study, we have also discovered that dispersion-enhanced radiation pressure and new forms of artificial electrostriction (with 10^6-fold increase in phonon-photon coupling) can be created with properly designed photonic crystal media. Through this research, we develop experimental and theoretical platforms for the systematic study of these novel physical effects.

Summary of Accomplishments:
Our most significant accomplishment through FY 2011 includes the theoretical prediction and experimental demonstration of stimulated Mach-wave emission within nanoscale suspended waveguides. Through the newly developed optomechanical device platform, we have experimentally demonstrated efficient generation both 4 GHz and 8 GHz phonons with light. This system has the following unique distinctions: 1) it is the first system to demonstrate stimulated Brillouin scattering in silicon, 2) it is the first demonstration of forward stimulated Brillouin scattering on a chip, and 3) the stimulated Brillouin gain of this system is larger than any known system to date.

We have published 4 conference papers, 2 journal papers and 1 journal paper is currently under review. Our work has lead to 3 invited conference presentations and 1 invited Journal paper. Several additional papers are in manuscript form and will be published in the coming months. Additionally, through the new concepts and theoretical models developed under this project, we have been awarded a follow-on

Defense Advanced Research Projects Agency (DARPA) project. This new project has allowed us to also develop formal collaborations with Massachusetts Institute of Technology (MIT) and Rockwell Collins for optomechanical technology development.

In arriving at these experimental results, we have made numerous theoretical discoveries and developed powerful new experimental capabilities including the following:

1. The first ever multi-scale models of photon-phonon coupling (micro- and nano-scales) leading to predictions of radically enhanced nanoscale polystyrene-b-polybutadiene-b-polystyrene (SBS) and novel forward SBS processes.
2. Novel theoretical treatments of optical forces at nanoscales have yielded fundamental scaling laws for optical forces due to the effects of electrostriction and radiation pressure, and forces in effective media.
3. The development of hybrid E-beam photolithography process with MEMS release enabling nanoscale lithographic patterning over entire wafers.
4. The development of novel spectroscopy techniques for precise determination of photon-phonon coupling for frequencies <40 GHz.

Significance:

Technologies for efficient and broadband conversion of signals from optical RF to phononic domains would enable a new class of chip-scale true time-delay and RF signal processing systems, greatly benefiting Sandia's missions by yielding improved RADAR, light detection and ranging (LIDAR), and synthetic aperture radar (SAR) performance. The optical-mechanical interactions will also lay the foundation for development of ultraprecise optically sensed seismometers, accelerometers/gyros, and strain sensors for navigation and structural health monitoring applications.

Refereed Communications:

P.T. Rakich, P. Davids, and Z. Wang, "Scaling of Optical Forces in Dielectric Waveguides: Rigorous Connection Between Radiation Pressure and Dispersion," *Optics Letters*, vol. 36, pp. 217-219, January 2011.

Z. Wang and P. Rakich, "Response Theory of Optical Forces in Two-Port Photonics Systems: A Simplified Framework for Examining Conservative and Non-Conservative Forces," Invited paper for Collective Phenomena Focus Issue in *Optics Express*.

Photodefined Micro-/Nanostructures for Sensing Applications
151337

Year 1 of 3
Principal Investigator: R. Polsky

Project Purpose:
The advancement of materials technology toward the development of ultrasensitive sensors for the detection of biological and chemical agents has been a long-standing challenge. The purpose of this project is to explore various lithographic techniques to make structures in photoresist and Ormocer® materials and explore chemical and material modifications to design novel sensing platforms. The key attributes that we intend to explore are as follows: 1) pattern structures for sensing applications using interference lithography (IL) and direct laser writing two-photon fabrication techniques, and 2) explore methods to improve the interfacial chemistry of the electrode surface to immobilize recognition elements, signaling pathways, anti-fouling components, etc. including nanoparticle and conducting polymer modifications. The resulting electrode can be tailored for specific applications and integrated into sensing platforms for the detection of chemical and biological threats.

Summary of Accomplishments:
We have characterized the deposition of palladium nanoparticles onto IL-fabricated 3D porous carbon and demonstrated control over the morphology of the final particle, which we tailored for non-enzymatic glucose detection. Platinum particles were also explored as oxygen sensors. Bimetallic alloy deposition followed by dealloying the less noble metal was explored to create nanoporous gold films. We also demonstrated that the substrates could be used as surface-enhanced Raman substrates after silver sputtering with enormous enhancement factors (up to 10^9). Stereolithography was used to create hollow-bored microneedles which we integrated with electrodes for novel in vivo transdermal electrochemical sensors. Carbon fibers were used to detect ascorbic acid and hydrogen peroxide. Additionally a bicomponent microneedle was created to detect glucose and glutamate.

Significance:
Both the basic science and the multidisciplinary engineering aspects of this project are in alignment with several laboratory missions. In addition to sensor applications, the proposed pyrolytic carbon/ Ormocer® structures find potential application in water purification, filtration/preconcentration of chem/bio agents, energy storage (Li^+ batteries, ultracapacitors), fuel cells, and hydrogen storage. Additionally, the ability to fabricate carbon structures with wavelength scale periodicity has enormous potential impact as a structured emitter/absorber for fields as diverse as energy harvesting and thermal signature management.

Refereed Communications:
X. Xiao, G.A. Montaño, T.L. Edwards, C.M. Washburn, S.M. Brozik, D.R. Wheeler, D. B. Burckel, and R. Polsky, "Lithographically Defined 3D Nanoporous Nonenzymatic Glucose Sensors," *Biosensors and Bioelectronics*, vol. 26, pp. 3641-3646, April 2011.

X. Xiao, J. Nogan, T. Beechem, G. A. Montaño, C.M. Washburn, J. Wang, S.M. Brozik, D.R. Wheeler, D. B. Burckel, and R. Polsky, "Lithographically-Defined 3D Porous Networks as Active Substrates for Surface Enhanced Raman Scattering," *Chemical Communications*, vol. 47, pp. 9858-9860, August 2011.

S. Sattayasamitsathit, A.M. O'Mahony, X. Xiao, S.M. Brozik, C.M. Washburn, D.R. Wheeler, J. Cha, D.B. Burckel, R. Polsky, and J. Wang, "Highly Dispersed Pt Nanoparticle-Modified 3D Porous Carbon: A Metallized Carbon Electrode Material," *Electrochemistry Communications*, vol. 13, p. 856-860, August 2011.

P.R. Miller, S.D. Gittard, T.L. Edwards, D.M. Lopez, X. Xiao, D.R. Wheeler, N.A. Monteiro-Riviere, S.M. Brozik, R. Polsky, and R.J. Narayan, "Integrated Carbon Fiber Electrodes Within Hollow Polymer Microneedles for Transdermal Electrochemical Sensing," *Biomicrofluidics*, vol. 5, pp. 013415,1-14, March 2011.

J.R. Windmiller, G.Valdés-Ramírez, N. Zhou, M. Zhou, P.R. Miller, C. Jin, S.M. Brozik, R. Polsky, E. Katz, R. Narayan, and J. Wang, "Bicomponent Microneedle Array Biosensor for Minimally-Invasive Glutamate Monitoring," *Electroanalysis*, vol. 23, pp. 2302-2309 October 2011.

Theoretical and Experimental Studies of Electrified Interfaces Relevant to Energy Storage
151338

Year 1 of 3
Principal Investigator: C. C. Hayden

Project Purpose:
Major advances in electrochemical technologies for energy storage require improved understanding of electrolyte/electrode interfaces, including structure, interfacial species, and electrochemical processes, and the incorporation of this understanding into quantitative models. Such models will guide development of advanced designs and materials to increase efficiency and reduce aging and failure rates. Simplified models such as Helmholtz's electric double-layer (EDL) concept and even Gouy-Chapman-Stern's diffuse model fail to take into account the molecular nature of ion distributions, solvents, and electrode surfaces, and therefore, cannot be used in predictive, high-fidelity simulations for device design. (Important aspects of the simulations include charge transfer rates, cycle lifetimes, and long-term stability.) We propose to develop detailed models of the structure and chemical properties of representative electrified interfaces, validated by multiparameter, minimally invasive experimental measurements. Such synergistic interaction between calculations and experiment is only now becoming possible with Sandia's rapid development of atomistic-to-continuum interfacial modeling and recent advances in spatially precise in situ optical probes enabled by emerging laser technology.

The project will ultimately provide a deep fundamental understanding of the molecular nature of charged interfaces which will benefit the modeling and design of practical systems. However, success demands development of new capabilities from both modeling and experiments to enable accurate treatment and characterization of length scales ranging from meso- to nanoscale. The optical diagnostics in some cases will be required to resolve nanometer distances, far below the diffraction limit of 0.25–0.5 micron. The calculations must treat molecular-scale features in the compact inner layer of the EDL, but must also range over mesoscale distances to capture ionic distributions within the diffuse layer. However, we believe the technical risk is justified in view of the potential for gaining a leadership position in predictive modeling and unique diagnostics for electrochemical interfaces.

Summary of Accomplishments:
This project integrates experimental optical measurements with theoretical modeling to provide fundamental understanding of molecular-scale structure of electrochemical interfaces. For experimental optical studies of interfaces, we have constructed a combined Raman and second harmonic generation microscope. Initial measurements provided high-quality, spatially resolved Raman spectra from various samples. To create transparent metallic interfaces suitable for optical measurements, we have grown micron-scale single crystal gold particles attached to indium tin oxide substrates for electrical contact. To introduce optical probes into the interface self-assembled monolayers (SAMS) is an approach that has been well characterized by standard electrochemical methods. We have developed SAMs functionalized with organic dyes for resonance Raman measurements and have synthesized 12-mercaptododecanenitrile to introduce cyano group Raman active probes into SAMs. Recently, we have also installed a polarization modulation reflection absorption infrared spectrometer (PM-RAIRS) for direct infrared interfacial absorption measurements with submonolayer sensitivity. We have two significant accomplishments in the modeling of the electrical double layer. First, we have built a preliminary molecular dynamics (MD) model of salt-water on gold at high voltages, which captures some of the experimental set-up. Most importantly, the model is able to capture the key aspects of the double layer: the immobile or Stern layer adjacent to the electrode, and a more diffuse layer further from it. We have computed some important quantities, such as the double layer's capacitance, which can be

compared to experimental measurements. A publication presenting these results is in preparation. The second accomplishment is that we have verified our electric field model for MD is appropriate for this type of problem. This has lead us to begin adding more physically realistic boundary conditions and constitutive relations to the electric field model, which will more accurately reflect experimental conditions.

Significance:
The research is relevant to DOE's mission in energy efficiency and energy security. The fundamental understanding of electrochemical interface properties will enable designs of future energy storage and conversion devices that operate with improved efficiency, enable the use of alternative energy sources, and reduce foreign imports of petroleum. Newly capable optical techniques along with the special experimental platforms will provide abilities for unprecedented in situ characterization of key molecular properties of electrified interfaces. These advances will support missions of the DOE's Basic Energy Sciences Condensed-Phase Interfacial Molecular Science project and goals of the recently announced innovation hub on electrical energy storage.

Refereed Communications:
J.A. Templeton, R.E. Jones, J.W. Lee, J.A. Zimmerman, and B.M. Wong, "A Long-Range Electric Field Solver for Molecular Dynamics Based on Atomistic-to-Continuum Modeling," *Journal of Chemical Theory and Computation*, vol. 7, pp. 1736-1749, May 2011.

Developing Thermoelectric Cryo-Cooling
151339

Year 1 of 3
Principal Investigator: D. L. Medlin

Project Purpose:
Many Sandia systems require low-temperature cooling near 77 K, including space-based-electronics for remote-sensing/verification projects, and terrestrial-devices such as photon-detectors, mirrors, integrated circuits, and chem-bio sensors. However, conventional cryogenic-coolers are large, expensive, high powered, and difficult to integrate with electronics. On-chip, solid-state thermoelectric (TE) cryo-cooling can reduce cost and inefficiencies, enabling future systems.

TE performance requires a high figure-of-merit, zT, optimized by high electrical conductivity, high thermopower, and low thermal conductivity — properties found in Bi-based alloys. However, commercial state-of-the-art materials are limited to zT ~ 1, too low for real cooling applications that must constantly remove heat from a power source. Recent reports of nanostructured bulk materials have shown zT ~ 1.6, largely through reduced thermal conductivity. Further advances demand corresponding improvements in electric conductivity and thermopower. Theory predicts 10-fold zT improvements in one-dimensional nanowires (diameters < 5 nm), due to quantum confinement, which creates peaks in the electronic density-of-states that enhance thermopower. Nevertheless, the present performance of nanowires is abysmal: the best reported zT = 0.12. A detailed literature review suggests that this failure is due to inadequate attention to key materials factors (composition and crystallinity) affecting the electronic transport.

The purpose of this project is to enhance thermoelectric performance at cryogenic temperatures using nanowires optimized for structure, composition, and dimensionality through an integrated program of synthesis, characterization, and theory. We will use novel electrochemical deposition approaches to provide the necessary materials control. We will employ advanced microscopies (atomic resolution transmission electron microscopy and atom probe tomography) to thoroughly evaluate material composition and structure, and we will measure the resulting transport properties on individual nanowires using novel probe platforms, guided by past theory and new modeling of nanoscale transport processes. Finally, we will fabricate and test cooling modules from TE nanowire arrays to establish the practical feasibility of this approach for cryogenic cooling.

Summary of Accomplishments:
During the first half of FY 2011 we have progressed toward our initial goal of achieving bulk-like properties in large-diameter BiSb nanowires. Our first step has been to refine our nanowire template procedures to better control the reliability and uniformity of the pore distributions. Key steps have been to improve our control of stress in the aluminum anodization layer and to implement a tungsten valve-layer approach to control the termination of the pore formation. In parallel, we have developed the electrochemical procedures and chemistries required to deposit Bi-Sb of appropriate composition and uniformity in nanowire geometries. This accomplishment has required overcoming several challenges. First, the slow reduction kinetics for Sb compared with Bi pose difficulties for compositional control. Second, the low conductivity of dimethyl sulfoxide (DMSO) and the high reduction potential of the $SbCl_3$ salts typically used for such electrochemical baths can cause significant non-uniformities. To solve these problems, we have replaced the $SbCl_3$ salts with SbI_3 salts, which have much lower reduction potentials. We have also added $LiClO_4$ as a supporting electrolyte, increased our counter electrode area, and explored masking controlled areas to improve the deposition field uniformity. We have also used high current density strikes to improve the initial nucleation density to ensure uniform

pore filling. We have now succeeding in achieving target compositions for Bi-Sb and have successfully grown nanowires of uniform composition (following the strike layer) and correct crystal structure.

Over the remainder of this fiscal year, we will work to improve our control of grain structure in these materials and perform transport property measurements. We will draw on advances in transport modeling to help in interpreting these measurements. As a step towards this goal, we have developed and published an analytical model describing the dependence of nanowire Joule heating on the surrounding environment.

Significance:
Advanced TE materials performance will enable new technologies for cooling and power generation that are relevant to the national security missions of DOE and other agencies, including DoD and DHS. Potential applications include new solutions for cryo-cooling to improve the performance of critical electronic systems for various detectors (optical, microwave, RADAR, chem-bio, etc.), as well as enabling new technologies for long-lived power sources for remote unattended operations.

Refereed Communications:
F. Léonard, "Reduced Joule Heating in Nanowires," *Applied Physics Letters*, vol. 98, pp. 103101-103103, March 2011.

Improving the Electrical and Thermal Resistance of Nanoscale Contacts
151340

Year 1 of 3
Principal Investigator: R. E. Jones

Project Purpose:
A fundamental factor limiting the performance of electronic and optoelectronic devices is the thermal and electrical resistance of the ubiquitous metal-semiconductor contact. This problem becomes more acute as devices move toward the nanoscale where these interfacial resistances increasingly contribute and are typically a source of device failure either during fabrication or later in service. While these effects have been studied extensively and are relatively well understood in bulk contacts, much of the physics must be re-evaluated for metal-nanostructure contacts due to the low dimensionality affecting central parameters such as electrostatic interactions, strain, and interfacial energies. Pragmatically, this reconsideration is warranted as bulk techniques for improving contact properties, e.g., heavily doping the semiconductor, have been shown to be ineffective or inappropriate for contacts to low-dimensional structures. Moreover, the techniques that do work, e.g., high temperature annealing, are not always reliable nor completely understood leading to a cookbook approach to fabrication.

In response, we propose a research effort that will discover the determining factors governing electron and phonon transport at contacts to single and arrayed nanotubes and nanowires. The combined experimental, simulation, and theory thrusts will establish the fundamental physics of nanoscale contacts that will enable the realization of controllable contacts to nanostructures.

Despite a problem of immense technical and scientific importance, there is very little literature on the mechanisms determining electrical and thermal contact resistance at the junctions of metals and nanostructure and some of it is extremely simplified. In fact, a large part of the more sophisticated existing literature has been authored by members of this team. Arising from these simplifications, an integrated theoretical-experimental approach to investigate electronic, thermal and electron-phonon processes at a nanoscale metal-semiconductor junction has not been attempted. Our integrated approach should then engender new models and discover new phenomena specific to the physics of nanodevices.

Summary of Accomplishments:
In our first year, we have made a number of advances. We have also met most of our milestones, unmodified, and have made significant progress toward all milestones.

In the electron transport process arena, we have fabricated devices and performed preliminary current-voltage measurements on single nanowire devices. We have also simulated the potential barrier in carbon nanotube devices due to unscreened charge near the contact interface (this work has been submitted to Applied Physics Letters). In addition, we have set-up a random phase approximation (GW) simulation of an embedded contact and discovered that the high-symmetry configuration used in the literature may give misleading results. This work should lead to a high-impact publication.

In the phonon transport arena, we have performed a focused ion beam cross-section of a metal-nanowire contact and preliminary electron microscopy using the same device used in the current-voltage measurements. On the simulation side, we have developed an adequate metal-semiconductor potential and have done preliminary simulations of phonon transport across rough interfaces. These results show that roughness of coherent/void-less interfaces behave contrary to expectations. We have a related work in the review process in *Physical Review B*. In the electron-phonon coupling arena, we have fabricated nanowire mats of various surface densities suitable for ultra fast Raman and transient thermoreflectance experiments. In addition, we have preliminary data showing that electron-phonon coupling increases with interface roughness and that controllable changes to the adhered atoms in a graphene-gold interface can lead to significant changes in the electron-phonon coupling.

In addition to the three publications in press this year, we have five more in preparation and have set up three important collaborations with Stanford University, the University of Indiana, and the University of Virginia.

Significance:
Sandia's surety, nonproliferation, threat detection, and energy missions are increasingly looking toward nanoelectronics for solutions. This project will address and potentially alleviate a fundamental roadblock in fabricating reliable, high-performance (current and frequency), nanoelectronic devices of all types. Specifically, this project seeks to provide science-based solutions to guide the design and fabrication of nanodevices in order to accelerate their technological integration.

Refereed Communications:
A.W. Cummings and F. Léonard, "Electrostatic Effects on Contacts to Carbon Nanotube Transistors," *Applied Physics Letters*, vol. 98, p. 263503, June 2011.

X.W. Zhou and R.E. Jones, "Effects of Cutoff Functions of Tersoff Potentials on Molecular Dynamics Simulations of Thermal Transport," *Modeling and Simulation in Materials Science and Engineering*, vol. 19, p. 025004, July 2011.

P.E. Hopkins, J.C. Duda, and P.M. Norris, "Anharmonic Phonon Interactions at Interfaces and Contributions to Thermal Boundary Conductance," *Journal of Heat Transfer*, vol. 133, p. 062401, June 2011.

Advanced High-Z NanoScintillators
151341

Year 1 of 3
Principal Investigator: B. A. Hernández-Sánchez

Project Purpose:
Scintillators detect radiation by producing light upon exposure; unfortunately, the current detection quality suffers from performance and reliability issues (i.e., low luminosity, volume restrictions, chemical instability). Important to overcoming these constraints are the elucidation of radiation interaction mechanisms for scintillating materials at multiple length scales (nano-micro-meso) and the discovery of novel high-Z nanoscintillators for gamma-ray detection. The goal of this project is to determine the utility of size-selected high Z transition metal chalcogenides (MEx, E = S, Se, Te) as novel scintillating materials. Without these improved scintillator materials, the correct identification/detection of radiation sources continues to be a vulnerability to the US.

For the scintillation community to fully embrace nanomaterials and ultimately attract outside agencies, it is important that fundamental materials research be undertaken addressing the optimal crystallite size (nano-meso) and the development of new materials. Once accomplished, direct sponsorship from a variety of sources that have already expressed interest becomes more likely. The development of novel scintillation materials and nanoscintillators is neither widespread nor established. Several key aspects prevent industry and academic pursuits: 1) single-crystal growth techniques used to validate a material's performance for gamma-ray spectrometers — this restricts materials examined; 2) lack of theoretical/fundamental radiation-detection physics occurring in materials are still under debate which precludes research in nanomaterials; and most important, 3) limited access to radiation characterization facilities. With its multidiscipline interactive researchers, Sandia is ideally suited to improve scintillators using existing expertise and capabilities to address key materials, characterization, and production of scintillator devices. Existing scintillator issues will be overcome by: 1) systematically evaluating oxide scintillator size effects (nano-meso); 2) developing novel size controlled scintillators based on unexplored high-Z transition metal chalcogenides; 3) exploring activator concentration on properties; and 4) developing nanocomposite materials for device development. The expected results promise to revolutionize current scintillator detector capabilities.

Summary of Accomplishments:
To produce the next generation of scintillator materials, it is important to determine the particle size effects on scintillation properties and how the radiation detection mechanisms differ from bulk (particulate size or crystalline symmetry or morphology). During year one, we focused on MWO_4 nanoscintillators synthesis, began to probe particle size effects on scintillation properties, and initiated investigation on the differences between nanoparticles and bulk scintillation behavior. We have discovered, through preliminary results, that size effects are occurring in scintillation behavior.

Determining the Size Effects on MWO_4 Scintillators — Synthesis of MWO_4:

- Developed new synthetic routes to generate complex ceramic metal tungstate (MWO_4) nanoparticles using solution precipitation and solovthermal techniques. Produced an entire family of known and not-so-well-known scintillators (MWO_4, M= Na, Ca, Ba, Sr, Pb, Cd).
- Based on previous work, the following commercially available precursors (e.g., nitrates, acetates, $W(OCH_2CH_3)_6$, $W(OCH_2CH_3)_5$ were explored.
- Micron scaled (MWO_4, M= Na, Ca, Ba, Pb, Cd) was purchased and (MWO_4, M= Ca, Pb,) were synthesized.

- Full characterization on MWO_4 nanoparticle size, morphology, composition, and surface chemistry was performed using electron microscopy and x-ray diffraction. Routes formed nanorods (Pb, Cd), wires (Cd), and dots (Na, Ca, Pb).

Characterize Scintillation Properties:

- Used ion beam induced luminescence, cathodoluminescence, and photoluminescence to characterize scintillation behavior (nanoparticle literature is limited to photoluminescence).
- Preliminary results indicate that with ultraviolet (UV) excitation, photoluminescent emission/excitation wavelengths shift between nanoscaled and micron scaled tungstates (i.e., 20-nm shift for $CaWO_4$; 13-nm shift for $PbWO_4$)
- Ion beam induced luminescence with proton excitation (mimic of neutron radiation) demonstrates different emission wavelengths, than with UV excitation, for both micron and nanoscaled materials.
- Cathodoluminescence of micron-sized powders indicate increased electron energy produces increased luminescence intensity. Luminescent emission wavelengths were similar to those observed with photoluminescence.

Significance:

High-performance scintillators are urgently needed for homeland security, nonproliferation, and event tracking operations to safeguard the US and its allies from radiological/nuclear threats. This research would provide the necessary R&D foundation needed to advance radiation detection capabilities that employ nanocrystalline, polycrystalline materials, composites, and other engineered materials to overcome the limitations of single crystal materials. This will advance Sandia capabilities to address the mission for monitoring activities associated with international nuclear safeguards and nuclear weapons treaty verification.

Tailoring Thermal and Electric Transport Properties Through Solid-State Self-Assembly
151343

Year 1 of 3
Principal Investigator: J. Ihlefeld

Project Purpose:
The purpose of this project is to develop a viable high-impact energy scavenging method based on the thermoelectric effect in materials composed of nontoxic and abundant elements and that are stable in air to high temperatures. Currently, the best moderate-temperature range (ca. 0 to ~800 °C) thermoelectrics are semiconductors composed of relatively toxic, rare, and strategically limited p-block elements (i.e., tellurides, antimonides, and selenides). Many oxide materials would meet requirements for large-scale impact; however, their thermoelectric figures of merit ($ZT=TS^2/rk$, where T is the temperature, S is the thermopower, r is the resistivity, and k is the thermal conductivity) must be improved for viability. The pervasive challenges for oxide thermoelectrics are low electronic conductivity and high thermal conductivities. To date, the field of oxide thermoelectrics, particularly for n-type materials, is in relative infancy. Only a few groups have investigated these materials, with virtually all groups focusing on single-phase homogeneous ceramics, thin films, and single crystals.

Stemming from recent reports of improved thermopower in highly reduced oxide ceramics with increased carrier concentrations and phonon scattering in defective regions and separate reports of decreased thermal conductivity in oxide films with complex layered atomic arrangements, we propose to combine the benefits of these two separate studies through two approaches: 1) by developing oxide ceramics with self-assembled nanostructured phases with controlled carrier concentrations, boundary geometries, and boundary concentrations, and 2) by designing new oxide materials where the mechanisms controlling electronic and thermal conductivity occur on separate crystal sublattices — a so-called phonon-glass electron-crystal. These methodologies have yet to be investigated by other researchers for thermoelectric applications in oxide materials — those that are environmentally benign and abundant.

Summary of Accomplishments:
We prepared $SrNbO_3$-based Ruddleson-Popper phase materials and measured their thermal conductivities. We have observed an 80% reduction in thermal conductivity from 7.5 W/m K to 1.5 W/m K through the formation of an n=3 phase (3 perovskite layers between SrO layers). We measured thermal conductivity in $SrTiO_3$ with grain sizes ranging from 100 to 42 nm. A 40% reduction with thermal conductivity was measured with room temperature values ranging from 6 to 2.3 W/m K observed.

We observed pseudo-spinodal decomposition in $Zn(Ga, Mn)_2O_4$ in epitaxial thin films. The study of single crystals with compositions including the two end-members and a 50/50 Ga/Mn composition will enable the role of the composition-mediated nanostructure on thermal and electrical properties to be isolated. Bulk ceramic materials of the same compositions have also been prepared and pseudo-spinodal decomposition observed.

We prepared dense single-phase 4% and 10% La-doped $SrTiO_3$ ceramics using a hybrid nanopowder/chemical solution deposition approach. The same approach will be scalable for the dopant studies.

We investigated the role of non-stoichiometry (cation vacancies) on the thermal conductivity of perovskite single-crystal $BiFeO_3$. Stoichiometric material possessed a room temperature thermal conductivity of 3 W/m K that was reduced to 2 W/m K through the introduction of 10% bismuth vacancies. $BiFeO_3$ is isostructural with $SrNbO_3$ and $SrTiO_3$ and is a model system to study vacancy effects owing to a broad single-phase field and availability of samples. Likewise, the formation of the Ruddleson-Popper phase of $SrNbO_3$ requires the formation of A-site vacancies in the perovskite layers.

Significance:

Thermoelectric energy conversion has wide applications for both cooling and power generation technologies relevant to DOE, NNSA, and broader national security needs. Our focus on oxide-based thermoelectric materials is particularly relevant to high-temperature power generation applications such as waste-heat recovery for improved energy efficiency and high-temperature radio-isotope-thermal generators for long-lived autonomous power sources. More broadly, by providing fundamental insights concerning thermoelectric transport in nanostructured bulk materials, this work should have general impact across the spectrum of thermoelectric technologies.

Our studies into the features that alter thermal conductivity in oxide thermoelectrics may have broad impacts to the general S&T community by providing fundamental information necessary to develop designer thermoelectrics.

Understanding and Controlling Low-Temperature Aging of Nanocrystalline Materials
151344

Year 1 of 3
Principal Investigator: C. C. Battaile

Project Purpose:
Nanocrystalline metals offer exceptional properties, e.g., high strength, fatigue resistance, radiation hardness, and low friction. The greatest roadblock to applying these materials is the fact that their grain structures evolve at ambient temperatures, and recent evidence indicates that nanocrystalline metals can even evolve at cryogenic temperatures faster than they do at room temperature. This can degrade properties and even accelerate failure. For example, large grains initiate fracture during fatigue of nanocrystalline nickel coatings, and coarsening of nanocrystalline copper lines in integrated circuits degrades their electronic properties. Low-temperature grain growth remains a mystery. Microstructures are usually stable below about 40% of the melting temperature. This is the case because the grain boundary velocity, v, equals the product of the driving pressure, p, and the boundary mobility, M, which decreases exponentially with temperature. Using parameters measured in aluminum, the velocity of nanoscale grain boundaries is about 40 µm/s at 70% of the melting temperature, but only 10^{-9} µm/s at room temperature. At cryogenic temperatures, the boundaries should not move perceptibly within the lifetime of the universe. So how can we explain, and ultimately control, ambient-temperature grain growth in nanocrystalline materials? Solving the mystery of ambient growth will require new understanding of, not only both the boundary mobility and driving pressure, but also how they interact in the microstructure. The proposed work utilizes Sandia's unique capabilities for studying microstructure evolution. New, high-throughput, low-temperature molecular dynamics (MD) simulations can uncover the mechanisms underlying this phenomenon. Polycrystal plasticity finite element modeling (PPFEM) will predict nanomechanical-driving pressures. Mesoscale grain growth simulations will integrate these results to reveal how they act in concert to cause ambient grain growth. Room- and cryogenic-temperature indentation and tension experiments will validate the simulations. These results will guide the design and synthesis of nanocrystalline films with improved low-temperature stability.

Summary of Accomplishments:
In the first year of this project, we have accomplished a number of notable achievements that impact our goals and milestones, only some of which are detailed here. We have demonstrated, for the first time, the evolution of nanocrystalline copper after indentation in liquid helium, i.e., at 4 K. In addition, we have performed nanoindentation experiments under a variety of other conditions and in other material systems to help identify the fundamental mechanisms of low-temperature grain growth. These experiments suggest that the presence of nanotwins in the microstructure is crucial for promoting the evolution of the microstructure during (or after?) indentation. Using molecular dynamics calculations, we have not only performed a survey of the temperature-dependent mobilities of a large variety of grain boundaries to identify which types of interfaces are potential candidates for low-temperature migration, but also successfully performed simulations of grain growth in nanocrystalline copper indented at only 0.2 meters per second and room temperature. We also performed simulations of deformation in nanotwinned crystals to demonstrate that nano-twins could enable grain coarsening by funneling dislocations to the grain boundaries.

Significance:
Nanocrystalline metals have exceptional properties, and are candidates for future weapon components (e.g., stronglink discriminators and mesosprings), energy applications (e.g., next-generation nuclear reactors and lightweight hydrogen containers), and computer chips (e.g., nanograined copper

interconnects). The possibility of an unforeseen disaster from an undiscovered aging mechanism is of grave concern, and requires the rigorous scientific exploration proposed here in order to understand the limits and applicability of these novel materials. Our S&T activities are constantly striving to avoid technological surprises. We never want to experience the unexpected from our key engineered components and systems.

Epsilon Near-Zero Material for Electromagnetic Energy Transport Through Subwavelength Channels
152504

Year 1 of 2
Principal Investigator: G. Subramania

Project Purpose:
Efficient transport of electromagnetic energy through subwavelength channels in the optical regime can dramatically enhance the performance of subwavelength imaging, photovoltaics, sensing and light emission. Current approaches based on plasmonic structures or negative index metamaterials tend to be lossy due to material absorption and have a small bandwidth due to reliance on resonance behavior. Here we propose using epsilon-near-zero (ENZ) material to achieve efficient subwavelength electromagnetic energy transport. ENZ materials have near-zero dielectric constant (epsilon) in the effective medium limit, resulting in an unusually large effective wavelength even at optical frequencies, thus enabling energy squeezing and transfer through subwavelength channels with lower losses over larger bandwidth. ENZ material has been investigated theoretically and experimentally in the microwave regime but remains a challenge in the optical regime due to difficult nanofabrication requirements. Experimental realization in the optical would enable a whole new generation of nanophotonic systems. We propose an approach of combining materials with negative (e.g., metal) and positive (e.g., SiO_2) dielectric constants to obtain materials with an effective bulk ENZ. We will explore theoretically and experimentally, in one dimension, the potential and limitations of this approach in subwavelength energy transfer and emission modification of nanoscale emitters. Basic understanding obtained in the one-dimensional system will be important for implementation in higher dimensions.

ENZ materials provide a powerful, innovative route to achieve broadband, subwavelength energy transport with low loss by exploiting the previously untapped vanishing dielectric constant regime. Current experimental work is mainly in the microwave regime. Since metal dielectric properties are considerably different at microwave frequencies, experimental demonstration at optical frequencies is a significant step both from a scientific and practical standpoint, rather than a mere extension. Many important applications enhanced by ENZ occur in the optical regime, especially the possibility of ultrasmall optical nanocircuitry to one day surpass Moore's law limitations.

Summary of Accomplishments:
We have designed a one-dimensional implementation of ENZ structure based on a metal-dielectric multilayer stack. We selected Ag for the metal due to its high plasma frequency and low loss. For the dielectric component we explored SiO_2 and TiO_2 as possible materials. Based on finite difference time domain simulations, we discovered that TiO_2 was more suitable than SiO_2. We learned that a smaller thickness of TiO_2 is sufficient compared to SiO_2, resulting in a multilayer structure that better approximates the ideal effective medium. Guided by simulations, we fabricated a 5-pair Ag/TiO_2 stack by alternating the deposition of Ag and TiO_2 using electron beam evaporation. We performed optical transmission and reflection measurements which compare well with simulations in their spectral response. The measured transmission magnitude is somewhat lower than that predicted from simulations. This is expected due to deviation in the thickness and the optical properties from those of the nominal values. In order to determine the ENZ wavelength of the structure, we have designed an interferometric experiment to measure the phase difference between light passing through a different thickness of ENZ medium. By measuring this phase difference as a function of wavelength and comparing it to a theoretical model, the ENZ wavelength can be determined. This experiment is currently in progress. Since an important goal of this project is light transport through subwavelength channels, we have explored theoretically, a structure consisting of a periodic array of subwavelength

double groves etched into a thin Au film. We have demonstrated that this structure enables electromagnetic energy to be squeezed to an area $(lambda/500)^2$ across a broad wavelength range. A nonresonant mechanism wherein the charges in the metal respond instantaneously to the incoming EM field is responsible for this behavior.

Significance:

Control and efficient electromagnetic energy transport through subwavelength channels at optical frequencies is a key scientific challenge that affects many areas of photonics such as photovoltaics, sensing subwavelength imaging and light emission. All these areas are significant and closely linked to DOE's mission of energy independence (e.g., photovoltaics and efficient lighting) and national security (e.g., sensing, imaging). The results obtained, thus far, realize an ENZ structure operating in the visible (i.e., fabrication of metal-dielectric multilayer structure, optical transmission properties) is an important step towards understanding their capabilities and limitations. This will enable to us evaluate their potential for achieving realistic devices predicted for these materials, including compact sensors and optical nanocircuits. For instance, all optical nanocircuitry is expected to be considerably faster, compact, and less energy consumptive than electronic circuits. A theoretical exploration in collaboration with the University of Exeter, UK, into achieving subwavelength energy transport has resulted in powerful and unexpected insights. We discovered through this theoretical study of light propagation in periodic, subwavelength double grooved slits that it is possible to funnel EM energy through an area as small as $(lambda/500^2$ across a broad wavelength range (e.g., 3–20 µm). The conventional approach has been to utilize resonances to achieve such effects as extraordinary optical transmission through subwavelength hole arrays that tend to operate in a narrow wavelength band with low transmission. The results obtained here (to appear in *Physical Review Letters*) indicate that a nonresonant mechanism, wherein the charges in the metal respond instantaneously to the incoming EM field, enables a broadband wavelength response with higher transmission. These results are significant and can substantially improve sensitivity of sensors and detectors as well as enhance nonlinearity that are important for security applications.

Refereed Communications:

G. Subramania, S. Foteinopoulou, and I. Brener, "Nonresonant Broadband Funneling of Light via Ultrasubwavelength Channels," to be published in *Physical Review Letters*.

High-Mobility 2D Hole Systems for Quantum Computing Applications
152505

Year 1 of 2
Principal Investigator: L. A. Tracy

Project Purpose:
One of the leading candidates for a solid-state quantum bit is the spin of a single electron confined in a semiconductor. Coherent control of individual electron spins has already been demonstrated in quantum dots. These groundbreaking experiments utilized high-mobility 2D electron systems in GaAs/AlGaAs heterostructures grown via molecular beam epitaxy (MBE). The major source of decoherence in such experiments is coupling between electron spins and nuclear spins in the host GaAs semiconductor. It has been proposed that hole spins in GaAs would be better suited for such experiments due to a lesser coupling between hole and nuclear spins. Recent experiments already show that the dephasing time for hole spins in GaAs quantum dots is at least one order of magnitude longer than that of the electron spin. One of the main reasons that there are relatively few experiments on holes in GaAs, as compared to electrons, is the difficulty of growing high-quality 2D hole systems (2DHS) that can be used to fabricate stable hole nanostructures (such as quantum dots). However, recent advances in growth of 2DHS via carbon doping provide a new possible route to obtaining material of comparable quality to current high-mobility 2D electron systems in GaAs. Building on successes in carbon doping of (100) oriented GaAs/AlGaAs heterostructures, we propose to develop 2DHS to enable experiments investigating the physics of hole spins in GaAs, with eventual application in the area of quantum computing.

Summary of Accomplishments:
We met all of our milestones for FY 2011, as follows:

- We demonstrated a 2D hole system with a mobility of about a half-million cm^2/Vs at a density of 6.5 x 10^{10} cm^{-2}. This mobility corresponds to a hole mean free path of about 1 micron, which is larger than the typical dimensions of a nanostructure such as a quantum dot or quantum point contact. Therefore, we expect to be able to fabricate quantum structures where the motion of the hole will not be impeded by the presence of defects.
- We have measured magnetotransport in our 2D hole system at T ~ 300 mK. We observed the quantum Hall effect, with plateaus in the Hall resistance and deep minima in the longitudinal resistance that correspond to exactly what we expect for a single 2D layer.
- We have demonstrated the ability to control the 2D hole density with surface gates. We have already fabricated quantum point contact (QPC) structures and measured the conductance versus gate voltage at T = 350 mK. The data shows some hints of steps due to conductance quantization, however, the positions of the steps indicate that the conductance is not perfectly ballistic. We plan to improve this by increasing the hole density or by decreasing the depth of the hole layer. This would help to maintain a higher mobility inside the QPC constriction.

Significance:
As an investigation of the basic physics of 2D hole systems, this work will have relevance to DOE’s mission of scientific discovery and innovation. This work may also provide new capabilities in the area of quantum information, a research topic with potential applications in secure communications, with possible additional relevance to DHS’s mission of improving cyber security.

Nanofabrication of Tunable Nanowire Lasers via Electron- and Ion-Beam Based Techniques
153346

Year 1 of 2
Principal Investigator: Q. Li

Project Purpose:
There is a strong desire to reduce the volume of semiconductor diode lasers to the minimum dimension in order to enable ultracompact and low-threshold coherent light sources. These compact light sources can be readily integrated with various micro-device platforms. The purpose of this project is to create tunable nanometer scale lasers using GaN and InGaN nanowires. Such nanolasers could enable a host of impactful and diverse applications including nanometer scale optical interconnects, ultrahigh density data storage, nanolithography, quantum computing, cell probes, and biochemical sensing as well as imaging. However, control of the optical emission properties of nanolasers is difficult due to a number of factors, including challenges of controlling nanowire material uniformity, optical gain, dimension, defect density, and morphology. Additionally, diffractive optical loss in the nanowire cavity creates a limit to the wire dimension to about 150-nm diameter. The desire to realize an electrically injected nanowire laser put additional constraint to the modal control. We propose to develop a novel nanowire synthesis route for creating high-quality nanowires with precisely tailored properties. We plan to manage optical loss through modal control using novel distributed feedback (DFB) schemes onto a single nanowire. The research direction proposed here has not been explored before largely due to difficulties in synthesizing high optical gain III-nitride nanowires with superior material quality and precisely control geometries. We propose to overcome these difficulties by developing top-down nanowire synthesis techniques and using high-resolution electron beams and ion beams to assist in the creation of novel nanometer-scale DFB structures on these nanowires.

Summary of Accomplishments:
GaN nanowires synthesized by vapor-solid-liquid mechanisms and a novel top-down technique were compared. We found that the top-down technique provides GaN nanowires with significantly improved materials quality, repeatability, uniformity, and optical performance. This top-down process is based on masked plasma etch of planar III nitride thin films and a unique wet etch process for creating non-tapered nanowires. Based on experimental measurement and Monte Carlo simulations, we found that these top-down nanowire arrays tend to be dislocation-free as their diameter is reduced below 150 nm. Most importantly, this top-down technique allows us to create uniform arrays of nanowires with precisely controlled nanowire length and diameter, which are important for manipulating the optical modes in the nanowires. We discovered single mode lasing behavior in the top-down GaN nanowires when their geometries are properly controlled. This single mode lasing was believed to be due to the high optical gain as well as mode completion. Moreover, low lasing thresholds were repeatedly measured from these top-down GaN nanowires. Based on the guidance provided from finite difference time domain simulations, several types of Distributed Bragg Reflector (DBR) and DFB structures were successfully created on the nanowires with electron beam and focused ion beam assisted techniques. Currently, we are continuing the nanowire laser fabrication and optical measurement to understand the physics of lasing mode control and lasing threshold reduction in these nanowires with novel DBR or DFB structures. Milestones in FY 2011 from the initial project have been achieved. So far, we published 3 conference presentations (*Electrochemical Society* 2011, *Materials Research Society* 2011, and *Electronic Materials Conference* 2011) and an invited article in SPIE Newsroom. We have a manuscript ready for submission to *Applied Physics Letters*. We are also editing a high impact manuscript, which we plan to submit to *Nature Nanotechnology*.

Significance:
This research effort is the first step to realize practical applications of electrically injected nanowire lasers. Leveraging the integration strength of Sandia, these nanowire lasers can be integrated with microfluidic devices, microelectromechanical system (MEMS), or other microsystems. In these components, the nanowire lasers provides coherent light sources in ultraviolet and visible ranges. With these light sources, we may be able to realize a photoluminescence system or a Raman system on a microchip. In the war against terrorism, these compact components can be used as in situ trace chemical and biochemical detection and analysis.

Besides its significance in Sandia's national security mission areas, this research effort is of importance in understanding the fundamental science of the interactions between light and matter. This work directly targets the main challenges in materials science, nanotechnology, and optoelectronics. Tunable nanowire lasers would also significantly impact DOE and national security missions by enabling an ultracompact, low-threshold, coherent UV-visible light source that could be integrated into numerous nano-and microsystems such as atom-chip sensors. New functionalities could be enabled in the integration of electronics and photonics, chem-bio detection and sterilization, solid-state lighting, ultrahigh density storage, and high-resolution imaging and lithography. New understandings of light-matter interactions in nanostructures would impact other mission-critical areas such as energy harvesting. DOE Basic Energy Sciences (BES), Energy Efficiency and Renewable Energy (EERE), Advanced Research Projects Agency - Energy (ARPA-E), Defense Advanced Research Projects Agency (DARPA), Defense Threat Reduction Agency (DTRA), and DHS are agencies that would have a potential interest in such capabilities.

Time-Resolved Chemical Mapping of Phase Transformations in Li-ion Battery Electrodes
153892

Year 1 of 2
Principal Investigator: J. D. Sugar

Project Purpose:
In order to make battery technologies a more attractive energy storage alternative to carbon-based fuels, we must increase their capacity, charge/discharge rates, and improve safety. All of these performance criteria are limited by the answer to this question: What controls how the ionic charge carriers enter and leave the electrodes? Although electronic and ionic conductivities are an important part of answering this question, equally important considerations are the rate-limiting steps in the electrode phase transformations. These delithiation reactions involve a structural transformation that could be limited by diffusion, surface-attachment, or strain. To date, these electrode reactions have mostly been investigated ex situ, and the intermediate steps must be interpolated from available data. An in situ observation of the transformation could provide the missing information but requires complex sample preparation techniques and a quantitative analytical approach for observing Li^+ ions to determine definitively which mechanisms dominate the charge storage dynamics. To differentiate between the different possible dominant mechanisms, we will develop in situ analytical capabilities in the transmission electron microscope (TEM) and a thin-film battery design so that the microscopic details of the phase transformation can be observed as they occur.

There has been much recent interest in developing in situ TEM platforms that can observe nucleation and growth or reaction phenomena. There has been little attention, however, to developing microanalytical capabilities that can also operate in situ. This work develops a capability to perform analytical energy-filtered TEM (EFTEM) in situ, which allows quantitative chemical measurements of battery electrode reaction kinetics at the nanoscale. This work is also developing a thin-film battery platform that can be cycled inside the TEM by applying a bias without the need for a special environmental cell. Combined, these two activities create high-risk, cutting-edge work that has the potential to revolutionize the current understanding of how to optimize battery electrode materials for higher capacity, charge/discharge rates, and safety.

Summary of Accomplishments:
In the first year of this project, we have done most of the preparatory work that will provide a higher chance of success in the second year. We have performed electron energy loss spectroscopy (EELS) on powders of $LiMn_2O_4$ and $LiFePO_4$, typical battery electrode materials. We have compared the EELS spectra from material that is completely lithiated with material that has been completely chemically delithiated by soaking it in a solution of NO_2BF_4 in acetonitrile. The comparison of EELS spectra allowed us to identify how the spectral shapes of Li, Fe, Mn, and O change when the electrode material is fully charged and discharged (or delithiated and lithiated). We used a combination of energy-filtered transmission electron microscopy (EFTEM) and multivariate statistical analysis (MSA) to identify the spatial distribution of Li. We developed a technique that allows us to combine data from the low-loss region and the core-loss region of the EELS spectrum so that we can associate changes in the shape of the Mn and O absorption edges with the shape of the Li edge in the plasmon region. We have successfully developed a technique to make battery cathodes by making a colloidal suspension and painting or electrospraying material onto an electrolyte substrate. We have successfully tested these batteries using cyclic voltammetry and impedance spectroscopy and learned how to identify battery redox reactions in the voltammogram. Finally, we have successfully fabricated our first TEM sample

and electrically connected it to an in situ e-chip using the focused-ion beam tool. This enables us to electrochemically cycle the sample inside the TEM.

Significance:

Reducing our reliance on foreign carbon-based fuels and having a secure and sustainable supply of resources is essential to national security. A profound understanding of the basic mechanisms underlying battery electrode phase transformations will allow the design of safer materials with faster charge/discharge rates, higher capacities, and longer lifetimes. Electrical energy storage problems are important to many agencies within DOE, including NNSA, Energy Efficiency and Renewable Energy (EERE), or Basic Energy Sciences (BES). Industrial partnerships are also possible.

On-Chip Low Power Frequency Comb with Spectral Selectivity
154081

Year 1 of 2
Principal Investigator: R. Camacho

Project Purpose:
On-chip wavelength division multiplexed (WDM) networks for next generation ExaFLOP computing and optical interconnects lack efficient "optical power supplies" for the thousands of laser frequencies needed. Millimeter-wave (100 GHz) sensors and secure communications approaches lack small, low-power means of generating the required complex waveforms. Ultrafast optical switching and logic remains an unrealized goal due to lack of a viable micro-integration path. This research will lay the foundation to address these needs by leveraging Sandia's silicon photonics platform to bring nonlinear optics to the chip-scale.

To focus this work, we will use optical nonlinearities (four-wave mixing) in silicon nitride to construct on-chip, low power, ultranarrow linewidth frequency combs compatible with complementary metal-oxide-semiconductor (CMOS) processing. This chip-scale comb-generator will convert single-frequency input laser light into an array of equally spaced laser wavelengths which can then be routed and processed by on-chip WDM networks, or used in ultrastable (fsec) timing sources, fast spectroscopic sensors, and arbitrary radio-frequency (RF)-photonic waveform generators. We will integrate new insights in multi-frequency selective high-Q resonators and develop the theoretical and simulation toolset to demonstrate chip-scale 40+ line comb generation at 50% improved efficiency. The ability to generate multiple narrowband wavelength sources on-chip in a CMOS-compatible process represents a significant advance in silicon photonics. On-chip optical signal generation is the final step to untethering chip-scale optical processing from bulky power supplies and laser sources for truly hand-held, low-power applications. Sandia already has an established high-functioning silicon photonics platform; this new technology would leverage existing capabilities and establish Sandia as an immediate leader in the field of microscale optical signal generation. The key thrust of this project will be to develop a rigorous scientific foundation for the on-chip nonlinear processes necessary for comb generation (all current Sandia silicon photonics components rely on linear processes), and develop a design space within processing and material constraints.

Summary of Accomplishments:
During the first eight months of this project, we have made three significant advances toward the realization of an on-chip multiwavelength laser source: 1) We have performed a rigorous analysis of a variety of waveguide and coupling cross-sections and identified the ones that maximized optical coupling to the nonlinear ring, 2) Using a new modeling technique, we have designed device geometries capable of supporting zero group-velocity-dispersion modes, a necessary prerequisite for nonlinear spectral generation in azimuthal geometries, 3) We have performed time-domain analysis for multispectral synthesis showing that, if we can fabricate our chosen geometry, we will, in fact, generate a comb with the desired characteristics.

During the course of the research, we identified a major challenge: the ideal waveguide geometries required a silicon nitride film three times thicker than is currently possible in the Sandia microfabrication facility (fab). This began an intense exploratory effort for both alternative materials as well as novel fabrication techniques that would allow us to grow the film. The first attempt to grow a thick nitride film was a partial failure, with stress-induced cracks appearing at the edge of the film. Using what we learned from the first attempt, we are attempting a modified fabrication technique. In addition, we have identified other promising materials that are potential candidates to replace silicon nitride.

Significance:
Technologies for efficient generation of multiwavelength on-chip sources would greatly benefit Sandia's national security missions by yielding improved performance in applications such as wavelength-division-multiplexed (WDM) networks, light detection and ranging (LIDAR), and advanced metrology.

On-Chip Coherent Qubit Operations with Microfabricated Surface Ion Traps
154195

Year 1 of 3
Principal Investigator: C. Highstrete

Project Purpose:
Trapped atomic ion quantum bits (qubits) have been employed successfully for quantum information (QI) processing and are promising for quantum computation. Primarily, tightly focused laser beams have been used to address electronic energy levels of individual ions (single qubit operations) and motional modes of qubit subsets (multiqubit entangling operations). However, spontaneous emission and technical difficulties stabilizing laser frequency, phase, amplitude, and beam pointing have kept fidelities below fault-tolerant levels. Alternatively, microwave fields can be used to manipulate ion qubits based on the hyperfine-split electronic ground state. Such qubits portend higher fidelity because they are practically immune to decoherence by spontaneous emission and are readily addressed by highly stable microwave components. However, limited utility has been realized with these qubits because, for free space microwaves, the long wavelength precludes focusing, causing all qubits to be simultaneously addressed; and small field gradients on the atomic scale produce negligible coupling to motional modes. Utilizing state-of-the-art microfabrication techniques, microwave electrodes with subwavelength dimensions can be designed to localize fields and generate high magnetic field gradients to individually address qubits (by selective frequency shifting) and excite motional modes. Our intent is to design and integrate subwavelength microwave electrodes into ion trap chips and perform local single- and two-qubit coherent operations. While Sandia's Microsystems and Engineering Sciences Applications (MESA) facility is the world leader in surface ion trap microfabrication technology, a key next step is to perform coherent trapped-ion qubit operations. Sandia is uniquely positioned to develop and demonstrate on-chip, localized, and laser-less qubit operation technology.

Summary of Accomplishments:
The early project emphasis has shifted from developing lab capability for legacy devices to design studies of more sophisticated devices — originally the final project phase. Extensive modeling studies have been accomplished to investigate the feasibility of sophisticated on-chip microwave devices for laser-less ion qubit control. Studies have identified device designs to supply adequate magnetic fields within manufacturing constraints. Additionally, passive minimization of qubit zone crosstalk and active cancellation with multiple electrode control degrees of freedom have been studied. Code was written to calculate magnetic fields and gradients of surface coil elements and to simultaneously solve for zero field solutions at ion position. Preliminary designs were identified that are capable of zeroing field at ions while providing large field gradients, two important requirements for two-qubit gates. Work is ongoing to study integration into ion trap devices using microfabrication technology, specifically low cross-talk signal routing and impedance matching.

In light of the above emphasis, and because of lead times associated with the optical equipment, the emphasis of laboratory efforts this fiscal year has been redirected toward design and capability development. However, significant progress has been made toward the laboratory goals as well. The laser system for trapping Ytterbium was designed and installed. The remaining optics required for Ytterbium trapping and shuttling have been acquired and are currently being installed. A vacuum chamber has been acquired and modified for Ytterbium operations. Custom optical phase modulators required for coherent operations have been designed and acquired. Signal generators for controlling frequency and pulse shaping have been acquired and assembly of other electronics has begun. The extensive scripting code required for controlling electronics was accelerated and is now complete.

Significance:
In *A Federal Vision for Quantum Information Science (QIS)*, Office of Science and Technology Policy (OSTP) identifies QIS as “a family of potentially disruptive technologies” that has the potential to “enhance discovery and economic strength” thus warranting “a cohesive national effort to achieve and maintain leadership.” This research supports DOE’s goal, “Maintain a Vibrant US Effort in Science and Engineering as a Cornerstone of Our Economic Prosperity.” QIS supports DOE’s diverse technical goals with promise to solve relevant problems that are intractable classically. The relevance to intelligence missions develops “strategic partnerships to address broad national security requirements” and “apply our capabilities for other critical national security missions.” It specifically benefits Intelligence and Defense missions dependent on information technology and processing. Specifically, Intelligence Advanced Research Projects Activity (IARPA’s) Multi-Qubit Coherent Operations project explores the control of quantum operations in a multi-qubit environment, including qubit cross talk and control, coupling, and readout systems. There are also several relevant DoD mission-enabling research areas.

The main impact of efforts to date is that the project is truly developing into a springboard for technology advance at Sandia and for the quantum information science community. Since the concept development of this project, microwave control of ion qubits has become a very highly regarded technical approach to ion trap quantum information processing technical challenges by the community, both within and outside Sandia. Primarily, tightly focused laser beams have been used to address electronic energy levels of individual ions (single qubit operations) and motional modes of qubit subsets (multiqubit entangling operations). However, spontaneous emission and technical difficulties stabilizing laser frequency, phase, amplitude, and beam pointing have kept fidelities below fault tolerant levels. Alternatively, microwave fields can be used to manipulate ion qubits based on the hyperfine-split electronic ground state. Such qubits portend higher fidelity because they are practically immune to decoherence by spontaneous emission and are readily addressed by highly stable microwave components.

This project promises to not only develop a currently nonexistent coherent ion qubit control capability at Sandia, but also put Sandia in the forefront in this R&D area. The early results of this project have generated a solicitation for a major follow-on R&D proposal to an external sponsor. Initial reception of the project has been very positive and the outlook for external follow-on research is promising.

Characterization and Synthesis of Energy Storage Materials
155552

Year 1 of 1
Principal Investigator: D. Robinson

Project Purpose:
This work is associated with a Presidential Early Career Award for Scientists and Engineers (PECASE) to Prof. Ilke Arslan at the University of California (UC) Davis.

In metals that are nanoporous, every atom is within a few nanometers of the surface. These materials have the highest practical surface area, which allows for rapid surface reactions and storage of near-stoichiometric amounts of adsorbates at interfaces. The thermal and chemical stability of these materials imposes a practical limit, which is affected by the composition, pore geometry, and crystallinity of the material. Nanoporous palladium alloys are of particular interest for hydrogen storage and separation. Sandia is skilled in preparation of such materials with regular arrays of 2–3 nm pores.

Our initial plan was to use scanning transmission electron microscope (TEM) tomography to study these materials. Early in the project, we obtained access to a liquid cell TEM stage — one of few such cells in operation, and we had an opportunity to pursue a groundbreaking study that observes growth of individual nanoporous particles in a lyotropic liquid crystal template. We changed course in order to take advantage of this opportunity.

In some versions of the synthesis, regular pores are obtained, and in other cases, particles have disordered pores or are nonporous. Particles may start as individual seeds that grow conformally around filamentous surfactant micelles, or they may be formed from many seeds that move within the surfactant template and fuse with their neighbors. If the seeds grow too quickly, they may push the surfactant template aside and become nonporous, or a buildup of byproducts may disrupt the template and break the micelles. With the liquid cell, we can make direct observations of the growth process and identify the correct hypothesis from among these. That evidence will help us devise new synthetic schemes that avoid the mechanisms that lead to suboptimal porosity.

Summary of Accomplishments:
We compared electron beam-induced growth of palladium particles in water and within the surfactant template using the liquid TEM cell. In water, growth is rapid and unconstrained. In the surfactant template, we observe rapid formation of seed particles, but these appear to be relatively immobile, and continued growth is slow — so the hypothesized overgrowth mechanism appears untrue in this case. When the particles reach a certain size, they appear to become more mobile, likely because they are able to break through the filamentous micelles that surround them. After that, the particles can fuse with their neighbors. Breaking of micelles could be due to Brownian forces exerted by an irregular particle, local heating caused by absorption of beam energy by the particle, or by buildup of byproducts such as hydrochloric acid (HCl) that are slow to diffuse away and chemically disrupt the micelle structure.

While we now face a new set of more detailed questions, this has been a major advance in our understanding that is already of benefit to our synthetic efforts. For example, in separately funded work, we have developed a new generation of material in the early stages of characterization in which the micelles should be harder to break.

Significance:

This project contributed basic understanding of material interactions on the nanometer scale and contributed to development of next-generation hydrogen isotope storage materials. Nanostructured hydrogen storage materials have potential for wide-scale application of hydrogen used as a combustion fuel or as a charge carrier in metal hydride batteries. Their hydrogen kinetics will be much faster than bulk powdered materials, and absorption enthalpies somewhat tunable. Nanostructured noble metals are also proving to be highly efficient catalysts.

Solar Fuel Cell for Wastewater Treatment with Simultaneous H_2 Production
155797

Year 1 of 3
Principal Investigator: K. R. Reyes

Project Purpose:
The purpose of the project is to develop nanostructured composite semiconductors in order to solve the limiting factors of traditional photoanodes in comprehensive and synergistic approach. Solar energy represents a potentially clean, safe and limitless energy source, but its use at global scale would benefit from efficient conversion of the energy into a fuel to allow storage and distribution. The use of sunlight to split water is one initial possibility of storing solar energy in an energy carrier (hydrogen). For solar-to-hydrogen conversion, specialized semiconductors are needed to absorb sunlight and use the light energy to produce clean hydrogen. The principal problem is that there is not a single commercial material that is efficient as well as durable, non-toxic, and inexpensive. Metal oxides are good candidates, but their efficiency is jeopardized by three important factors: poor charge-carrier mobility, large bandgaps, and fast electron/hole recombination. A better electron/hole transport and collection is needed to increase the hydrogen production efficiency. We are proposing to develop organized nanostructures (e.g., TiO_2 nanotubes) to direct the flow of photogenerated charges more efficiently than nanoparticle networks, for instance. The electrons are directed though the vertical axis and the holes are collected though the horizontal axis of the nanotubes. To increase the sunlight absorption of TiO_2 (bandgap =3.2 eV), the nanotubes are coated with semiconductor with a narrower bandgap (e.g. WO_3, bandgap =2.6 eV). This composite WO_3/TiO_2 has the same ordered structure as TiO_2 nanotubes with an external WO_3 layer. The electron/hole recombination is also affected because water oxidation is a slow reaction. Aqueous organic pollutants will be used as hole scavengers to reduce the electron/hole recombination on the photoanode and consequently increase the hydrogen production on the cathode. This innovative photoelectrochemical system would have a high potential for clean hydrogen production as well as pollutant photodegradation treatment.

Summary of Accomplishments:
We developed a novel nanostructured composite semiconductor: WO_3/TiO_2 nanotubes and we set up an anodization station. First, we developed TiO_2 nanotubes by anodization using Ti foil as a substrate. The anodization parameters including sample preparation, anodization time, anodization potential and electrolyte were optimized to obtain the desired TiO_2 nanotube morphology. We analyzed the morphology of TiO_2 nanotubes using scanning electron microscopy (SEM). SEM results indicate that the nanotubes are highly uniform and vertically oriented with a length of 18 microns and a diameter of 100 nm. The nanotube walls are well defined with a thickness of around 5 nm. After annealing in air at 500 °C, the nanotubes show a very well defined crystal structure determined by x-ray diffraction. After the optimization of TiO_2 nanostructures, Tungsten was deposited atop the nanotubes by sputtering. Currently, we are optimizing the anodization conditions for the W coating layer. SEM results indicate that this composite WO_3/TiO_2 has the same ordered structure as TiO_2 nanotubes with an external WO_3 porous layer, which would be the absorbing semiconductor. Energy-dispersive x-ray spectroscopy demonstrated the presence of WO3. Diffuse reflectance spectra show an improvement in the visible absorption relative to bare TiO2 nanotubes. With these accomplishments, the two first milestones are completed. In addition, the WO_3/TiO_2 nanotubes were successfully transferred to a conductive glass (F-doped tin oxide). The freestanding WO_3/TiO_2 nanotubes are robust enough to keep their morphological features and allow a mechanical transfer to different substrates. A photoelectrochemical station with a solar simulator is under development. Photoelectrochemical experiments will be carried out to measure the important parameters, such as photocurrent density, fill factor, open circuit voltage,

and hydrogen production efficiency. In addition, photocatalytic experiments will be used to measure the degradation rate of organic pollutants.

Significance:
The S&T community has been very interested in the use of metal oxides for water splitting since the early 1970s when Fujishima and Honda demonstrated that single crystal TiO_2 can split water-using sunlight. However, the efficiency was very low for commercial uses due to the large bandgap of TiO_2. Extensive efforts to reduce the bandgap reported a promising increase in the sunlight absorption, however, the photoelectrochemical performance was even worse. These results indicate that the absorption is not the only limiting factor. In this project, we identified the three majors factors jeopardizing the efficiency of metal oxides: 1) poor charge-carrier mobility, 2) large bandgaps (Eg), and 3) fast electron/hole recombination. This project focuses on the manipulation of semiconductors to correct each of those limiting factors in a comprehensive and synergistic approach. The accomplishments of this project mean a new, simple, economical and reliable way to synthesize nanostructured composite materials with optimized performance for hydrogen production and photodegradation of organic pollutants.

The results of this project have a direct impact on Sandia's national security mission. The first mission in the DOE strategic plan is the energy security through reliable, clean, and affordable energy. Hydrogen is known as the fuel of tomorrow. Its use for vehicle and electricity generation cannot only reduce our dependence on imported oil, but also reduce emissions of greenhouse gases (two of the principal DOE Energy Security Goals). However, hydrogen should be produced from a clean, safe and renewable energy source. Solar water splitting is a very promising approach to produce clean hydrogen on a global scale.

Beyond the Ideal Nanostructure: Local Environmental Effects on the Electronic and Optical Properties of Carbon Nanotubes
157694

Year 1 of 3
Principal Investigator: D. C. Spataru

Project Purpose:
In the nanomaterials arena, carbon nanotubes (CNTs) have attracted tremendous interest for a number of applications, and also for their breadth of new scientific challenges. In most applications, CNTs are subject to external perturbations that make their behavior deviate from the ideal, isolated CNT case. Examples include a substrate, other nanostructures, polymers or DNA encapsulation, metallic contacts, doping, applied electric or magnetic fields, applied strain, etc. The electronic and optical properties of CNTs are expected to be altered by such environmental and dimensionality effects.

We will theoretically address how environmental effects impact the electronic and optical properties of carbon nanotubes. Employing ab initio methods that take into account many-electron correlation effects, we plan to study the influence of two important perturbations, substrate-nanotube interactions and proximity of plasmonic materials. Anticipating the change in properties of CNTs due to a substrate or plasmonic material is a crucial issue for the potential integration of CNTs into functional devices and a very interesting problem from a fundamental physics point of view. We are addressing important issues such as band gap renormalization in CNTs induced by a metallic substrate or enhanced photoabsorption rates of a CNT in the proximity of a plasmonic material. The embedding approach that we propose for describing long-range polarization effects may be used in other important problems such as chemical reactions at surfaces or in solutions.

Summary of Accomplishments:
We have worked out the theoretical framework needed to study, within an embedding approach — that relies on many-body methods — the electronic and optical properties of a generic nanomaterial (such as molecules, carbon nanotubes or graphene) physisorbed on a dielectric substrate or metal. We have completed the code development that allows studying the electronic properties of these nanomaterials in the case of a quasistatic environment. We have benchmarked our approach on a simple system, namely a benzene molecule physisorbed on a metallic substrate, and obtained very good agreement with full ab-initio calculations.

Significance:
The work proposed here addresses some fundamental challenges that have been identified by DOE in the control of material processes at the level of electrons. In order to achieve this goal, it is essential to understand the electronic and optical properties of nanomaterials, which inherently requires many-body ab initio approaches. These approaches fit well under the DOE theme for scientific discovery and innovation, where the study of electronic correlations and computational nanoscience and capabilities to link the nanoscale with larger length scales are important.

Microscale Heat Exchangers for Cryogenic Micro-Cooling Applications
158181

Year 1 of 3
Principal Investigator: A. J. Gross

Project Purpose:
There is a need to create new microscale heat exchanger structures in order to implement cryogenic cooling of low power microelectromechanical system (MEMS) and microelectronic devices. Development of high-performance microscale coolers will enable high-performance cryogenic sensors and electronics to be deployed in systems where their size and power consumption are currently prohibitive.

Cryogenic coolers capable of reaching temperatures of 100 K or lower often rely on Joule-Thomson (JT) or Stirling cycle cooling. Both types of devices require efficient heat exchangers. However, previous micro-JT and micro-Stirling coolers suffered from parasitic heat losses resulting from the fabrication techniques and materials used. Additionally, many of these devices have not been compatible with wafer scale integration. The current state of the art has therefore failed to address the need for a highly integrated and efficient solution to cryogenic cooling at the microscale.

The proposed work will address this problem through the development and demonstration of new structures that implement micro-fabricated heat exchangers for use in micro-scale coolers. This project will focus on implementing counter flow heat exchangers (CFHXs) and regenerative heat exchangers that have high efficiency and can be integrated into complete systems. It is differentiated from previous work by focusing on planar, thin film micromachining instead of bulk materials. A process will be developed for fabricating all the aforementioned devices, allowing for highly integrated micro heat exchangers. The use of thin film dielectrics provides thermal isolation, increasing efficiency of the coolers compared to designs based on bulk materials, and will allow for wafer-scale fabrication and integration. The process will be used to demonstrate a CFHX as part of a J-T cooling system for applications with heat loads less than 1 mW. The process technology will also be used to implement a microscale regenerative heat exchanger for use in a Stirling cooler.

Summary of Accomplishments:
A simplified model of a counter-flow heat exchanger has been developed. The model restricts the geometry to set of circular coaxial pipes, with hot, high-pressure flow in the inner pipe, and cold low-pressure flow in the outer pipe. It models the fluid flow analytically based on the steady state flow in a cylinder or annulus, and uses the calculated flow field to numerically solve for the temperature at steady state. By working in this simplified domain, the calculations can be performed quickly, and rapid iteration of a wide range of flow rates and geometries is possible. The simulations predict that with a mass flow rate on the order of 0.1mg/s divide among 20 parallel sets of pipes, a heat exchanger length of 5 mm, and inner pipe diameter of 10 µm and an outer pipe diameter of 30 µm will be sufficient to enable cooling below 120 K, when nitrogen is used as the working fluid.

Significance:
This work will directly support the science, technology and engineering mission of the DOE and Sandia by improving the state of the art in microsystems technology. Additionally, the micro cryocoolers proposed as the end result of the project would have applications in producing smaller, lighter, and more energy efficient high performance sensing systems for use in areas such as homeland security, defense systems and nonproliferation.

New Thin Film Materials for Electronics
158184

Year 1 of 3
Principal Investigator: A. M. Schwartzberg

Project Purpose:
This project details a research plan to develop and investigate novel thin film organic conductors with drastically improved electronic properties over the current state of the art. By leveraging the unique crystallinity of metal-organic frameworks (MOFs) and a novel Langmuir-Blodgett deposition technique, we will generate large area crystalline organic films for electronic applications on any substrate. We will develop a new set of characterization tools by both building capability at Sandia, and through the user facility at the molecular foundry at Lawrence Berkeley National Laboratory. We propose to develop a synthetic methodology for the growth of large area crystalline thin films of MOFs, currently impossible, and a set of imaging and spectroscopic tools including confocal and near-field Raman imaging, atomic force microscopy, electron microscopy, and scanning transmission x-ray microscopy, revealing ultrahigh resolution chemical information important to a complete understanding of film growth kinetics. While this technique and the resulting materials will be fundamentally different from current crystalline thin-films, many of the underlying questions remain the same: What is the nature of nucleation and how does it affect overall growth? How do defects form and propagate through the film? It is conceivable to propose mechanisms similar to those in ionic crystal growth such as catalytic nucleation, and lattice vacancies. We will use our expertise in spectral imaging and synthetic nanochemistry to answer these and other questions, and apply the results to improve materials growth. MOF thin films present great potential for revolutionizing solid-state bulk- and nanoscale device physics.

Summary of Accomplishments:
In the first two months of this project, the work has largely involved devising the techniques and preparing the facilities required to carry out this work. A user project for the molecular foundry at Lawrence Berkeley Labs was obtained to carry out the advanced optical techniques required and time to carry out initial trial x-ray microscopy measurements at the advanced light source. We have designed and rebuilt a Langmuir Blodgett (LB) trough and written software to drive and control the time sensitive kinetic measurements necessary. We have begun the studying the synthetic process to form MOF thin films on LB surfaces, however, this study is not yet complete. We have begun imaging work with a similar thin film molecular material, peptoid sheets. We have shown the first ever high-resolution (<300 nm) confocal Raman images of these ultrathin (<3 nm) materials. In addition, we have incorporated fluorescent tags into the peptoid sheets and performed subdiffraction limited near field fluorescence imaging, and have observed the first direct evidence of crystalline structure and packing. These initial optical measurements have confirmed that such measurements on one to two molecule thick films are possible, and will be transferred to the new MOF thin film materials upon completion.

Significance:
Crystalline MOF thin films will be a paradigm shifting material for energy research and, therefore, will have a direct impact on DOE's fundamental area of interest, specifically in clean energy and photovoltaics. These materials can help produce low-cost, high-efficiency photovoltaics due to the high processability and high conductivity, predicted to improve mobility by at least one order of magnitude over current organic electronic materials.

Cubic Organic Scintillators as Improved Materials for Fast Neutron Detection
158481

Year 1 of 3
Principal Investigator: P. L. Feng

Project Purpose:
Neutron and gamma particle discrimination in organic scintillators is achieved via comparison of the prompt and delayed components of the scintillation response, corresponding to fast fluorescence and triplet-triplet annihilation (TTA). A crucial factor that determines the extent of TTA and the efficiency of particle discrimination is the triplet mobility within a material, which is directly correlated with the molecular orientations and structure. Existing materials for pulse-shape discrimination (PSD) include liquid and low-symmetry crystalline organic scintillators, neither of which possesses the required degree of structural flexibility to understand the factors that control triplet mobility rates and the extent of TTA. Low-symmetry crystalline scintillators also suffer from anisotropic optical and mechanical properties that limit their practical application. In a bottom-up approach, we intend to synthesize different classes of cubic crystalline organic scintillators to study the structure-property relationships relevant to improved neutron/gamma particle discrimination. This approach is akin to noncovalent crystal engineering and is differentiated from current approaches to scintillator discovery that include top-down combinatorial and empirical methods. No cubic organic scintillators have been characterized to date.

This work seeks to elucidate the effects of crystallographic structure upon the transport properties and corresponding particle-discrimination performance of high-symmetry organic scintillators. This represents the first experimental investigation of the scintillation behavior of isotropic organic crystals. Additionally, diffusion rates have been characterized for Bloch states in cubic inorganic semiconductors such as Si and Ge, although no similar studies have been performed for cubic organic materials. This project thus has implications, not only for the design of improved PSD-capable scintillators, but also towards the design of new materials for improved charge carrier transport in organic photovoltaic applications. Furthermore, theoretical predictions of enhanced diffusion rates and reduced percolation thresholds in high-symmetry organic structures have yet to be explored and confirmed experimentally.

Summary of Accomplishments:
We synthesized and characterized the luminescence properties of the first targeted tri-aryl amine cubic organic scintillator: tris(1-naphthyl)amine. Initial multigram scale synthesis of this product was successful but revealed the presence of a strongly absorbing impurity, which we attributed to unreacted starting materials. These impurities were found to quench the luminescence and strongly color the obtained single crystals. We demonstrated effective purification of the desired product via iterative fractional recrystallization procedures, leading to transparent centimeter-sized single crystals that were found to be luminescent. Photoluminescence and scintillation testing revealed desirable properties for radiation detection applications, including blue emission (410 nm) and fast timing characteristics (2.2 ns). In addition to the above accomplishments, we also initiated the synthesis of additional cubic organic materials comprising aromatic phosphine oxides. Intermediate reaction products were isolated in good yields for these multistep chemical reactions.

A robust PSD characterization method was also developed for the rapid R&D testing of new organic scintillators, including microscale samples. This method employs a comparison of the pulse height versus pulse area or a ratio of prompt to delayed charge, which allows for significant flexibility in the acquisition parameters. The performance of this method was benchmarked against present PSD liquid scintillators as well as newly formulated PSD plastic scintillators developed at Sandia.

Significance:
The new materials developed in this work will benefit technologies for national security and nuclear nonproliferation, including detection systems for special nuclear materials. Anticipated benefits are 1) increased sensitivity for fission spectrum neutrons, 2) reduced detection thresholds due to increased triplet-triplet luminosity, and 3) elimination of hazardous material storage, transportation, and disposal. Agencies that have vested interests in neutron-sensitive materials include DOE and the Defense Threat Reduction Agency.

NEW DIRECTIONS INVESTMENT AREA

This investment area focuses on national security research fields into which Sandia has more recently embarked, and hence, tends to encompass initiatives that seek to draw existing Laboratories expertise into new applications for national security. Best exemplifying such initiatives are projects in biological sciences — with emphasis on alternative energy and biothreat reduction — projects at the nanotechnology-bioscience interface, and those in the cognitive sciences — particularly as applied to support for decision-makers.

From Benchtop to Raceway: Spectroscopic Signatures of Dynamic Biological Processes in Algal Communities
Project 141528

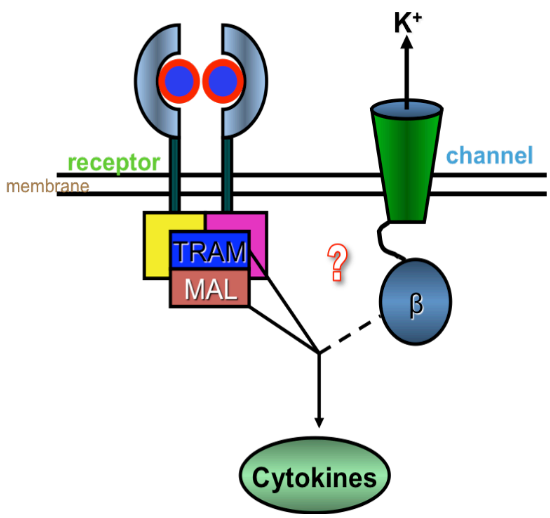
In support of the ultimate goal of industrial-scale cultivation of algae as a source of biofuels (particularly algal oils for biodiesel), this project is investigating fundamental knowledge gaps in algal biology, seeking to discover robust spectroscopic signatures correlated to algal health and photosynthetic efficiency/oil production at industrial scale in algal raceway cultures. A particular emphasis is on stressors found in the arid southwestern ecosystem, a potentials site of large-sale algal farms. In addition to automated biological and chemical monitoring as called for in DOE's *Algal Biofuels Draft Roadmap*, the project is attempting to develop predictive computational models of algal growth and productivity at the industrial scale.

Algal raceways, one method of industrial-scale cultivation of algae

K-Channels: On/Off Switches of Innate Immune Responses

130785

Immune responses encompass a complex array of cellular responses underpinned by molecular signaling and signal transduction. One key signal molecular transduction mechanism is the coupling of ligand-receptor binding events to the activation of potassium-ion (K^+) channels that mediate transmembrane flux of K^+. This "molecular switch" apparently modulates innate immune responses to attacks by pathogens, and utilizing Sandia's resources in microfluidics, molecular modeling, and high-resolution optical and electronic cell interrogation, this project has investigated the relationship between signaling molecules, channel proteins, and innate immune responses. In addition to the fundamental knowledge gained, it has set the stage for manipulation of immune responses via manipulation of channel proteins, potentially an important capability in biodefense against pathogens capable of pandemic-scale threats to human populations.



Schematic drawing of the coupling of an immune system receptor protein activated by a microorganismal signal (red-rimmed blue circles), in turn activating a K^+ channel that catalyzes outward K^+ flux and production of chemical messenger cytokines by the immune cell.

New Directions Investment Area

A Systems Biology Approach to Understanding Viral Hemorrhagic Fever Pathogenesis
130781

Year 3 of 3
Principal Investigator: B. Carson

Project Purpose:
Arenaviruses such as Lassa cause lethal hemorrhagic fever in humans and are pathogens of bioterror concern. They may be transmitted by airborne routes and have incubation times under two weeks with mortality up to 30%. A fundamental problem in understanding their pathogenicity is that infected and uninfected cells can exchange information, reciprocally influencing their behavior. Thus, cell population level experiments will never tell us why some people survive while others die from Lassa fever because many ill effects of viral infection are mediated by the immune system rather than by the virus itself. Excessive Type I interferons drive hemorrhagic symptoms, but arenaviruses paradoxically appear to block production of these cytokines. We hypothesize that this apparent contradiction is due to differential effects of the virus on the infected cell versus uninfected neighboring cells. We will deconvolute this system by microfluidically isolating and infecting individual cells then measuring cytokines with novel fluorescent transcriptional reporters and in situ staining. We will compare isolated cell to population level infection to discover how these viruses provoke lethal cytokine production. There are currently no means to accomplish the cell isolation required to differentiate cell-intrinsic from extrinsic effects, and thus, to address this fundamental question in host-pathogen biology. Although there are limited ways to block signaling through particular receptors, these are highly problematic and require prior knowledge of the signal involved.

Summary of Accomplishments:
We generated several new fluorescent reporter constructs useful for monitoring innate immune responses at the individual cell level, including cytokine promoter and transcription factor activity. We developed methods to use fluorescence in situ hybridization to detect viral infection and replication at the single-cell level on-chip. We made many improvements to our fluidic control systems used in cell capture and on-chip infection experiments. We developed low cost disposable valve and chip manifold systems to decrease cross-contamination and facilitate use of our system in biosafety level (BSL)-3/4 environments. We added automation capability to our imaging system to facilitate long-term high-time-resolution experiments. We developed three new chip designs with protocols for high-throughput on-chip infection experiments. We identified key sites within the Arenavirus nucleoprotein required for or involved in suppression of Type I interferon responses, as well as evidence that a second site yet to be characterized also is present. We developed a novel computational pipeline for predicting virus-host protein interactions and applied it to Pichinde virus nucleoprotein. We developed protocols and acquired equipment required for virus culture and purification, setting the stage for future work at Sandia in Virology. We submitted one manuscript for publication and will soon submit a second.

Significance:
This project benefits the DOE scientific and defense and DHS awareness and response strategic goals by addressing a key deficiency in our understanding of emerging infectious hemorrhagic fever virus pathogenesis. We will employ Sandia's highly evolved microfluidic technologies to develop biomarker assays of unprecedented sensitivity to study the response of individual cells to a National Institute of

Allergy and Infectious Diseases (NIAID) category A virus, ultimately supporting therapeutic and vaccine strategies to combat these viruses.

Biomolecular Interactions and Responses of Human Epithelial and Macrophage Cells to Engineered Nanomaterials
130782

Year 3 of 3
Principal Investigator: S. M. Brozik

Project Purpose:
Engineered nanomaterials (ENMs) are increasingly being used in commercial products, particularly in the biomedical, cosmetic, and clothing industries. For example, pants and shirts are routinely manufactured with silver nanoparticles to render them "wrinkle-free." Despite the growing applications, the associated environmental health and safety (EHS) impacts are completely unknown. The significance of this problem became pervasive within the general public when Prince Charles authored an article in 2004 warning of the potential social, ethical, health, and environmental issues connected to nanotechnology. The EHS concerns, however, continued to receive relatively little consideration from federal agencies as compared with large investments in basic nanoscience R&D. The mounting literature regarding the toxicology of ENMs (e.g., the ability of inhaled nanoparticles to cross the blood-brain barrier) has spurred a recent realization within the National Nanotechnology Initiative (NNI) and other federal agencies that the EHS impacts related to nanotechnology must be addressed now. We proposed to address key aspects of this problem by 1) developing primary correlations between nanoparticle properties and their effects on cell health and toxicity, and 2) establishing a basic understanding of the bimolecular pathways involved in the interactions and response of cells to nanoparticles. An important challenge embodied within this problem arises from the ability to synthesize nanoparticles with a wide array of physical properties (e.g., size, shape, composition, surface chemistry, etc.) which, in turn, creates an immense, multidimensional problem in assessing toxicological effects. We studied the cell-surface interaction and response pathways of epithelial cell lines that are involved in the toxicological response to nanoparticles of varying size and metal composition using advanced imaging techniques, biochemical analyses, and optical and mass spectrometry methods. Such fundamental discovery will provide the requisite foundation for developing risk-based predictive models for engineered nanoparticles and materials.

Summary of Accomplishments:
Significant progress was made in developing correlations between toxicity/response of immune cells and the size, surface functionality, and shape of quantum dots (QDs). Uptake and response of twelve different nanoparticles (Qdot 545, 565, 585, 605, 620, and 655; amine- and carboxy-functionalized) was quantitatively evaluated using brightfield and fluorescence microscopy. QDs exhibit different photoluminescent properties based on size and differential quenching in media. Therefore, we quantified the emission properties of each QD in the cell media and developed normalization factors to compensate for these differences and normalized the uptake measurements. Uptake was strongly correlated with the nanoparticle's aspect ratio with maximum uptake for rod-shaped particles (aspect ratio >2). No changes in cytokine release were observed at 24 hours post-QD exposure. Similar results were observed for S9 bronchial epithelial, T84 colorectal epithelial, and BeWo placental cells. Multivariate curve resolution (MCR) was used to resolve >5 QD spectral components and lysosomal dye from confocal images. This data showed that aspect ratio was correlated negatively with sequestration into lysosomal vesicles.

In another set of experiments, A549 human lung epithelial cells were exposed to varying concentrations of gold (AuNPs) and silver nanoparticles (AgNPs) of sizes 20 nm and 60 nm and their cytotoxic response was evaluated by measuring WST-1 activity, cytokine production of interleukins, IL-6 and IL-8, and the oxidative stress marker Heme oxygenase 1 (HO-1). Results of this study indicated a significant, nonlinear interaction between nanoparticle size and concentration (i.e., dose). Twenty-nm AuNPs and AgNPs elicited a significant IL-8 response (compared to negative control) at all concentrations while 60-nm AuNPs and AgNPs did not elicit IL-8 secretion above negative controls until a concentration of 10^9 particles/mL was applied.

Significance:
NNI has recognized the immediate and important need to establish a basic understanding of the health-related issues regarding engineered nanomaterials. Our studies addressed this challenge by establishing fundamental relationships between the physical and chemical properties of engineered nanoparticles and the associated biomolecular interactions and response of cells. Specifically, we were able to correlate diffusion and uptake of QDs by rat basophilic leukemia (RBL) cells to shape (aspect ratio) and size of the particle. In addition, the cytotoxic effect of gold and silver particles on human lung epithelial cells was shown to be dose dependent as well as size dependent; though the interaction was nonlinear.

The entry and interaction of nanoparticles into the human body has generated important scientific questions and an increasingly fearful perception within federal funding agencies and the general public. For example, the DOE has undertaken a strong, proactive commitment to the safe handling and disposal of nanoparticles at the five DOE Nanoscale Science Research Centers. The primary caveat is that the environmental safety and health recommendations are largely based on properties of the bulk materials and may not correlate directly with the intrinsically different properties of nanoparticles such as aspect ratio and size. Our results realize the importance of evaluating the various specific properties of nanoparticles.

Refereed Communications:
J.S. Aaron, A.C. Greene, P.G. Kotula, G.D. Bachand, and J.A. Timlin, "Advanced Optical Imaging Reveals the Dependence of Particle Geometry on Interactions between CdSe Quantum Dots and Immune Cells," *Small*, vol. 7, pp. 334-341, February 2011.

From Algae to Oilgae: In Situ Studies of the Factors Controlling Growth and Oil Production in Microalgae
130783

Year 3 of 3
Principal Investigator: S. Singh

Project Purpose:
Transforming algal oil into biodiesel requires solving the problems of growing large robust algae populations that produce high fractions of easily harvested specific fatty acids. It is generally believed that fatty acid composition and production vary among algal species and in response to altered environmental conditions. Current efforts to these ends proceed in engineering fashion, largely ignoring the fundamental biological processes in play. As a consequence, important issues regarding cell growth, utility of the fatty acids produced, and efficient oil recovery have been difficult to resolve. We will use our unique single-cell in situ experimental capabilities to develop fundamental, science-based insights into algal growth, triacylglyceride (TAG) production, and the relationship of these processes to photosynthesis and environmental factors.

Several problems associated with efficient lipid extraction and lack of reliable lipid characterization techniques have so far made it difficult to generate the multifactorial response curves necessary for an in-depth understanding of the connections between growth, photosynthesis, and lipid production pathways of alga. In particular, this proposal aims to clarify the results of previous ex situ observations of bulk cultures in the context of Sandia's technologically enabled in situ single-cell analyses.

The goal of this project, to generate the multifactorial map of environmental factors controlling algal growth and lipid production from single-cell analyses (hyperspectral fluorescence, Raman, x-ray tomography, and electrophysiology), requires unprecedented application of high-resolution technological approaches at throughput levels sufficient to describe the diversity of full algal colonies. This endeavor confronts a generally held sentiment among researchers that high resolution fundamentally excludes high throughput.

Summary of Accomplishments:
We discovered and demonstrated several unique approaches for analysis and postprocessing of high lipid producing microalga over the life of this project. These accomplishments include an in vivo Raman spectroscopy-based lipidomics assessment of algae (published, see below); high spatial resolution x-ray tomographic analysis of lipid production in algae (in preparation for *Science*); a label-free hyperspectral fluorescence method for determining lipid production based on fractional colocalization of lipid and carotenoid bodies (in preparation for *Journal of Biotechnology*); a generalized multiparametric analyses of photo-osmotic adaption using covariance analysis of 25 measured biochemical, photosynthesis, and biomass-related parameters (in preparation for *Biotechnology and Bioengineering*); a study that relates different mechanisms of nutrient depletion stress to physiological changes and lipid increase for optimized algal harvesting (in preparation for *Bioresource Technology*); and a study that details a one-step ionic liquid process for simultaneously lysing algal cells and separating the lipids and sugars (in preparation for *Journal of Biotechnology*). In addition to the publications listed above, three invention disclosures, two provisional patent applications, and one full patent application have been filed based on the potential for high-value intellectual property from findings that occurred over the course of this project. One of the invention disclosures has resulted in a successful Small Business Administration (SBA) grant in collaboration with a local instrument developer, Bay Spec.

Significance:
The development of a robust national supply of renewable biofuels is a priority for DOE. This research can enable Sandia's efforts to establish the most direct and competent procedures for selecting and optimizing algal biomass for biofuels through detailed in situ molecular-level understanding of factors affecting lipid production and composition. This work will complement current biofuel, energy-water nexus, and water desalination projects. Our project will lead to expanding the knowledge base at Sandia to support the biofuels mission and is envisioned to potentially lead to proposals and projects with DOE Office of Science, Energy Efficiency and Renewable Energy (EERE), and industry.

The value chain of algal biotechnology is widely believed to entail strategic developments in novel algal strains and feedstocks, and methods for harvesting and dewatering, drying and processing, chemical extraction and conversion, and commercial deployment. Key accomplishments were made through this project at several of the process levels involved in developing a robust biofuels industry based on microalgae. The highest priority discoveries relate to basic algal physiology and biochemistry that can be used to guide future engineering efforts. These findings have yielded important insight on how carbon is assimilated in relation to other nutrients, and how environmental stress channels carbon metabolism into various biochemical pathways. In the case of nutrient stress, we observe a decrease in production of proteins related to photoprotection, and a corresponding increase in lipid production. These effects were found to vary based on the rate of nutrient limitation stress, with dramatic changes associated with the largest increase in lipid yield. Other physiological correlations, including increasing cell size with increasing lipid should facilitate developments toward passive, size-selective harvesting. In the case of photo-osmotic stress, we observed increased carotenoid production as well as an unexpected lipid microparticle excretion phenomenon that may be employed for strategies focused on continuous direct lipid harvesting. Also in the realm of chemical extraction and dewatering, ionic liquids were found to be useful both for lysis of algal biomass and separation of the resulting carbohydrate and lipid fractions. Furthermore, multiple advances were made in the realm of diagnostics for monitoring biomaterials production and strain selection. These advances, including nondestructive in situ fluorescence and Raman measurements of algal lipid quantity and speciation, and spectroscopic characterization of photosynthetic productivity show considerable promise for determination of optimal nutrient conditions and temporal regimes for harvest, as well as selection of the highest performing individual cells for breeding purposes. Through these findings, we have developed a number of novel propositions for scalable strategies for algal biomass production that sidestep wasteful or inefficient practices that undermine the commercial use of algae as a biofuels feedstock.

Refereed Communications:
H. Wu, J.V. Volponi, B.A. Simmons, and S. Singh, "In Vivo Lipidomics Using Single-Cell Raman Spectroscopy," *Proceedings of the National Academy of Sciences of the USA*, vol. 108, pp. 3809-3814, March 2011.

K-Channels: On/Off Switches of Innate Immune Responses
130785

Year 3 of 3
Principal Investigator: S. B. Rempe

Project Purpose:
Infectious diseases from pathogenic microbes annually account for one-quarter of all deaths worldwide and, in a pandemic year, a single pathogenic strain can kill more than 2% of the world's population. Current efforts to stave off the "inevitable" next infectious disease pandemic focus on traditional prescriptions of developing new vaccines and drugs that kill microbes, with disappointing results. To progress, a new paradigm in medical treatment is needed for fighting infectious disease. Inspired by recent work, we will look to the immune cells, not the microbes, for potential drug targets.

Recent evidence suggests that a molecular switch exists in cell membranes that can actively modulate immune responses to pathogenic attacks. Unexpectedly, the switch exists in the form of a transmembrane channel protein that selectively catalyzes potassium (K^+) transport. We propose to investigate mechanisms of activating these transmembrane proteins involved in innate immune responses using a fundamental bioscience research and development strategy that capitalizes on our recent advances in molecular modeling, high-resolution optical and electronic cell interrogation techniques, and microfluidics platform development. With these unique methods, we will interrogate the relationship between signaling molecules, channel proteins, and immune responses with unprecedented accuracy and scope, ranging from the atomic resolution of single protein channels, to signaling processes of individual immune cells. The scientific insight gained should inform efforts to manipulate channel activity to boost or suppress innate immune responses, depending on the pathogen threat at hand. Our work supports Sandia's commitment to biodefense and emerging infectious disease and public health. We envision an innovative new strategy toward combating infectious disease: manipulation of specific immune responses via manipulation of channel proteins functionally linked to the immune response. Project creativity encompasses innovations in theory and spectroscopy to probe mechanisms of channel-tuned immune responses with unprecedented high resolution (single channels at atomic resolution) and broad scope (single proteins in live cells tracked optically and electrically).

Summary of Accomplishments:
In the first experiments ever performed in cell nutrient media, we demonstrated that outwardly rectifying transmembrane potassium channel proteins of macrophages are activated by the cell wall component of gram-negative bacteria, lipopolysaccharide (LPS). LPS stimulates cytokine production via known intracellular signaling pathways, and also enhances efflux of K^+ through potassium channels. We also demonstrated with a membrane potential fluorescence resonance energy transfer (FRET) probe that LPS stimulation of toll-like receptor (TLR4) in macrophages depolarizes the membrane, and formation of an activated TLR4 complex is associated with formation of a lipid raft. In the inverse experiment, we demonstrated that blocked potassium channels inhibit two hallmark events in TLR4 signaling:
1) blocked K^+ efflux from BK channels inhibits production of a cytokine promoter and 2) block of other K+ channels inhibited translocation of a nuclear transcription factor between nucleus and cytoplasm. We investigated how the immune challenging molecule, LPS, alters activity of the transmembrane channel protein after proposing a new hypothesis based on a 2010 paper in *Nature*. Noting that the receptor protein, TLR4, contains a leucine-rich-repeat chemical signature, we proposed the novel idea that LPS activates channels through colocalization with TLR4 via lipid raft formation, followed by activation by the leucine-rich repeats (LRR) chemical signature on the receptor, TLR4. So far, we showed with Fluorescence Resonance Energy Transfer (FRET) that TLR4 receptor and BK calcium-activated

potassium channels colocalize in transfected human embryonic kidney (HEK) cells, especially after chemically activating the channels. Further, we gained new insights into the mechanism of channel activation — by contraction of the gating ring rather than prior proposals of iris-like dilation. Finally, we developed a statistical theoretical framework for efficient, quantum analysis of channel function and a new framework for predicting channel current versus driving potentials based on extensible sets of information. Studies of the mechanism of channel deactivation by a model blocker suggest a new gating mechanism within the intracellular vestibule.

Significance:
If an infectious disease such as the feared avian influenza virus wiped out 2% of the world's population, with more than half of the dead constituting young adults between 18–40 years of age, then social stability, national and global economies, and military capabilities would likely disintegrate. Thus, advances made toward understanding innate immune responses to pathogenic infections, so that these may be manipulated for favorable therapeutic outcomes (as outlined in our proposed work), strongly support the DOE/DHS national security missions. Our new insights about how immune cell activation involves formation of receptor-channel complexes associated with lipid rafts, membrane depolarization triggered by the challenger molecule, membrane repolarization by enhanced activity of the channel, and how channel activity depends on structural changes in an intracellular vestibule can lead to new strategies for tuning immune responses via drugs that interfere with specific interactions unique to the channels important to cell signaling.

Refereed Communications:
S. Varma, D.M. Rogers, L.R. Pratt, and S.B. Rempe, "Design Principles for K^+ Selectivity in Membrane Transport," *Journal of General Physiology*, vol. 137, pp. 479-488, May 2011.

R.W. Davis, C.L. Kozina, H.D.T. Jones, S. Branda, M.B. Sinclair, S. Singh, and S.B. Rempe, "Environmental Perturbations to Fluorescent Proteins Allow Unambiguous Discrimination of Sequence Identical Constructs," to be published in *Physical Biology.*

S. Varma and S.B. Rempe, "Multibody Effects in Ion Binding and Selectivity," *Biophysical Journal*, vol. 99, pp. 3394-3401, November 2010.

D.M. Rogers and S.B. Rempe, "Probing the Thermodynamics of Competitive Ion Binding Using Minimum Energy Structures," *Journal of Physical Chemistry B*, vol. 115, pp. 9116-9129, July 2011.

D.M. Rogers and S.B. Rempe, "A First and Second Law for Nonequilibrium Thermodynamics: Maximum Entropy Derivation of the Fluctuation-Dissipation Theorem and Entropy Production Functionals," to be published in *Physical Review E*.

N.W. Gray, D.M. Rogers, S.B. Rempe, and E.G. Moczydlowski, "Destabilization of the Tetrameric Structure of the KcsA K^+ Channel by Local Anesthetics," to be published in *Biochemistry.*

Robust Automated Knowledge Capture
130787

Year 3 of 3
Principal Investigator: R. G. Abbott

Project Purpose:
Agencies in the national security domain need tools that enable modeling of human knowledge and behavior at a level of individual specificity that has been largely ignored within the cognitive neurosciences. For example, security simulations require models of adversaries who adaptively strive to defeat our defenses and safeguards. The Computer Science and Technology (CS&T) mission — understanding high-consequence decision-making under stress — cannot be achieved without better understanding strategy selection and adaptation. Automated Knowledge Capture (AKC) is the most promising avenue for supplying cognitive models tailored to differences in performance, decision -making, and learning in complex environments. A prevailing assumption in cognitive theory and related modeling has been that cognitive processes are largely invariant across individuals and across different conditions for an individual. Between-subject and within-subject variability is generally regarded as measurement error. We propose that cognitive adaptability is a trait necessary to explain the inherently dynamic nature of cognitive processes as individuals adapt their available resources to ongoing circumstances. This does not imply a "blank slate," or that humans are predisposed to process information in particular ways. Instead, this project asserts that, given variation in the structure and functioning of the brain, there exists inherent flexibility that may be quantified and used to predict differences in cognitive performance between individuals and for a given individual over time. A fundamental challenge in establishing cognitive adaptability is modeling individuals' relative strengths and weaknesses, and tendencies to adopt different strategies. Through previous investments by Sandia and the US Navy, Sandia has developed unique AKC capabilities that use machine learning to construct individualized models and is, thus, uniquely positioned to conduct the research necessary to advance Cognitive Adaptability Theory.

Summary of Accomplishments:
We developed a theoretically grounded model created to predict the likelihood that people will shift strategies during an ongoing task. This model incorporates both task-based and experience-based factors. The task-based factors are as follows: 1) changes in task demands, 2) suitability of the current strategy for the task, and 3) time on task. The experience-based factors are as follows: 1) whether a person has recently shifted strategies, 2) how often a person has shifted strategies, 3) how much planning a person has engaged in on the current trial, 4) whether there has been a decrease in performance, 5) whether such a decrease was a result of a shift to an inferior strategy, 6) whether a change in performance is an isolated event or spasm, 7) whether the person has been doing the task for a period without performance improvement, and 8) a person's propensity to switch strategies based on his/her history with the current task. The model was assessed using data from figure-drawing studies and a conceptually driven decision-making study, predicting strategy switching with an average of 84% accuracy.

We also conducted studies in multitasking, which has become increasingly prevalent in today's world and in most professions. Participants first completed a battery of individual differences tests of cognitive abilities followed by multitasking sessions with a flight simulator. The difficulty of the flight simulator was incrementally increased via three experimental manipulations. We found that scholastic aptitude and working memory predicted general multitasking ability (i.e., baseline difficulty), but spatial ability was the major predictor of adaptability in all three experimental manipulations. Cluster analyses were used to group individuals into one of five adaptability profiles: consistent performers, good adapters, poor adapters, attackers, and avoiders. Spatial ability, again, was the individual difference measure that discriminated the clusters.

Significance:
Sandia's AKC capabilities have already demonstrated value in several DOE and DoD applications including physical security, tactics training, and intelligence applications. However, the limiting factor in these applications is predictive accuracy of individual models in varied contexts and the inability to characterize the accuracy of these predictions. This research will distinguish AKC research at Sandia and supply hardware and software prototypes for future applications. Unique AKC capabilities will likely result in growth in existing collaborations that supply AKC for military and intelligence organizations, for applications currently including training systems and operator cognitive aides.

Refereed Communications:
M. Trumbo, S. Stevens-Adams, S.M.L. Hendrickson, R. G. Abbott, M. Haass, and C. Forsythe "Individual Differences and the Science of Human Performance," presented at the 14th International Conference on Human-Computer Interaction, Orlando, FL, July 2011.

M. Kalbfleish and C. Forsythe, "Instantiating the Progress of Neurotechnology for Applications in National Defense Intelligence," to be published in *Synesis: A Journal of Science, Technology, Ethics and Policy*.

C. Forsythe and J. Giordano, "The Need for a US Strategy Addressing Brain Science and Its Ramifications for National Security," to be published in *Synesis: A Journal of Science, Technology, Ethics and Policy*.

M. Zotov, C. Forsythe, A. Voyt, I. Akhemedova, and V. Petrukovich, "A Dynamic Approach to the Physiological-Based Assessment of Resilience to Stressful Conditions," presented at the 14th International Conference on Human-Computer Interaction, Orlando, FL, July 2011.

Construction of an Abiotic Reverse-Electron Transfer System for Energy Production and Many Biocatalytic Pathways
141524

Year 2 of 3
Principal Investigator: E. Ackerman

Project Purpose:
The guiding principles of all renewable energy production from biomass are the following: 1) the energy is in the high-density electron carriers, either organic (e.g., EtOH, butanol) or inorganic (e.g., H_2 or electricity); and 2) sunlight is the ultimate source of energy, powering photosynthesis to synthesize organic molecules. Converting biomass energy to fuels (concentrated electron carriers) is biochemically feasible and performed by many microbial and eukaryotic communities. Yet, the thermodynamic constraints of keeping cells alive mandate that energy yields from many pathways are, and will remain, suboptimal. Excess reducing equivalents are generated during metabolic reactions (e.g., bacteria channel two-thirds of their electron flow during glycolysis to make acetic acid rather than H_2). Overcoming the problem of excess reducing equivalents in living cells is a major bottleneck that must be overcome to increase yields. This project seeks to harness components of known metabolons derived from multiple species to ultimately create an abiotic reverse electron transfer (RET) system. Although many of the RET components will consist of proteins and cell-like and/or synthetic membranes, the core reaction centers will be enzyme based, albeit optimized for our abiotic system, rather than living organism(s). The work is difficult because: 1) not all components have been defined, even from living symbiotic systems surviving at the edge of what is thought to be the thermodynamically possible and 2) considerable recombinant cloning and expression of "difficult" proteins will be required. (Difficult proteins are those requiring considerable effort to express in active form in milligram quantities.) Since this system will be freed from sustaining life, we will have considerably more reaction design freedom, including unnatural amino acids, (electrically active) nanoporous materials, and artificial membranes. If successful, the approaches could revolutionize basic approaches to economically feasible bio-inspired reactions.

Summary of Accomplishments:
We are attempting to build non-living, bio-based reaction pathways that will overcome the thermodynamic limitations associated with living cells, especially the major problem of excess reducing equivalents generated during metabolic reactions. To synthesize the relevant proteins and their variants, we are using cell-free protein synthesis with wheat germ extracts. When coupled with our robotics, we can synthesize 384 proteins/day, including variants of single proteins. Unexpectedly, we had multiple difficulties producing proteins using our system and it took many months to find the cause of the problems. We solved the problem, tracing most of the difficulties to bad reagents. To do so, we had to prepare multiple plasmid preparations of control plasmids coding for proteins that we had either successfully produced previously, or new proteins that should not pose difficulties. Before making the proteins, we had to demonstrate that we could transcribe the coding regions of the plasmids into ribonucleic acid (RNA). It consumed some time to confirm that we made RNA transcripts of the correct sizes. Eventually, we were able to synthesize green fluorescent protein, organophosphorous hydrolase (OPH), and dihydrofolate reductase. Since these disparate proteins were synthesized successfully, we can now try to make proteins associated with energy generation and RET chain proteins. We also successfully noncovalently immobilized OPH in functionalized nanoporous materials and showed that it had enhanced activity and stability. It was even stable to the strong denaturant 0.05% sodium dodecyl sulfate (SDS) and tolerated diurnal cycles of temperatures ranging from –20 °C to +50 °C. Thus, once we have produced the relevant proteins for this project, we can stabilize them using the nanomaterials.

Significance:

Bio-based approaches to energy production, remediation, security-based sensors, and chemical syntheses all face the same thermodynamic limitations related to disposing of excess reducing equivalents. This project's R&D is relevant to all these missions because it could provide a general solution to utilizing valuable biologically based reactions. The ability to produce key reagents (proteins) is fundamentally important to many of the biology missions at Sandia in both the biofuels and biothreats arenas. Our high-throughput protein production technology is based on robotic methods that are readily applicable to these projects. New projects beginning in FY 2012 will also benefit from this technology that is becoming more widely used at Sandia. The ability to stabilize proteins in materials is also an important technology that aligns with the scientific vision for Sandia biology. Coupling the two technologies (high-throughput protein production with protein stabilization) is also relevant in discovering synergy and emergent behavior amongst communities of enzymes.

From Benchtop to Raceway: Spectroscopic Signatures of Dynamic Biological Processes in Algal Communities
141528

Year 2 of 3
Principal Investigator: J. A. Timlin

Project Purpose:
Microalgae are emerging as serious contenders for alternative energy biomass. Like lignocellulosic materials, there are major scientific challenges to an industrial-scale algal biofuels mission . Recently three broad areas of R&D needs have been identified for economically viable, industrial-scale cultivation of algae: 1) culture sustainability system productivity, 2) nutrient source scaling and sustainability, and 3) water conservation, management, and recycling. Progress in each of these areas is limited by significant knowledge gaps in fundamental algal biology. This project takes the first step toward addressing this shortcoming by applying a novel, multidisciplinary, multiscale approach that utilizes Sandia's expertise in bioanalytical spectroscopy, chemical imaging, remote sensing, genomics, and computational modeling to investigate the effects dynamic abiotic and biotic stressors have on algal photosynthesis, growth, and lipid production. This is a largely unexplored area of algal biology. Of particular note is the lack of research on the dynamic response to stressors encountered in the arid southwest ecosystem, a potential siting area of large-scale algal farms. The outcome of our project is fundamental knowledge of the underlying biological processes. We will use this new knowledge to: 1) discover robust spectroscopic signatures correlated to algal pond composition, algal health, photosynthetic efficiency, and oil production at scale, and 2) develop predictive computational models of algal growth and productivity at the industrial scale. Quoting the Algal Biofuels Draft Roadmap: "Methods for automated biological and chemical monitoring in production settings will be essential for assessing the health and compositional dynamics of algal ponds." Currently, monitoring is done with off-line measurements that are too slow and too sparse to provide the real-time process control required for efficient algal production in a large-scale algal raceway. The knowledge gained in this project will enable significant gains in productivity and sustainability that are important for optimizing industrial-scale algal facilities for cost-efficient algal biofuels production.

Summary of Accomplishments:
During FY 2011, we have continued our progress toward our goals of: 1) discovering fundamental knowledge about the dynamic response of biofuels-relevant algal species to stressors, 2) identifying spectroscopic signatures for health and productivity at the benchtop and greenhouse scale, and 3) developing a comprehensive computational model for algae growth in an open raceway. Major accomplishments include the following:

- Conducted benchtop experiments coupled with hyperspectral confocal microscopy to understand the effect CO_2-concentrating mechanism function has on lipid production and algal growth in *Chlamydomonas reinhardtii* (*C. reinhardtii*) and *Nannochioropsis salina* (*N. salina*).
- Designed and began experiments to elucidate the mechanisms of programmed cell death (PCD) in algae. Using sequences from *Arabidopsis thaliana* that are known to have roles in PCD, we mined putative PCD-relevant genetic loci from the model alga, *C. reinhardtii*, designed and optimized quantitative polymerase chain reaction (qPCR) primers for these loci. In a correlated effort, we have performed an initial screen using flow cytometry, optical microscopy, and two-photon excited fluorescence to identify physiological and morphological markers of PCD under variable abiotic stress conditions.

- Acquired temporal series of reflectivity measurements for *N. salina* growth cycles in both the laboratory and the greenhouse, and developed a spectroscopic model to interpret the data at both scales; lab-scale work was submitted for publication in *Algal Research*.
- Spectrally resolved beta-carotene and astaxanthin dynamics in *H. pluvialis* cells in vivo manuscript published in *PLoS ONE*.
- Completed a sensitivity study of algae growth parameters, determined species-specific constituent relationship necessary to refine our computational model. Through these efforts we have adapted the model to include effects of pH and then used this model to simulate our greenhouse experiments; a manuscript is in preparation.

Our team members have presented this work in the form of four presentations (three invited) and seven posters at conferences ranging from algal biofuels to the broader scientific community.

Significance:
Our work fills a strategic niche in an important, yet largely unexplored, area of biofuels where Sandia has unique capabilities. We have assembled a talented interdisciplinary team and are tackling key challenges described in the National Algal Biofuels Roadmap. This creative technical approach will provide Sandia with differentiating capabilities in algal biology addressing cultivation at scale and is a key step for Sandia's future missions in algal biofuels research. Our research is directly relevant to the current national security mission of DOE/Energy Efficiency and Renewable Energy (EERE) as well as the current and future interests of DOE/Biological and Environmental Research (BER) and Advanced Research Projects Agency-Energy (ARPA-E) programs.

Refereed Communications:
A.M. Collins, H.D.T. Jones, D. Han, Q. Hu, T.E. Beechem, and J.A. Timlin, "Carotenoid Distribution in Living Cells of *Haematococcus pluvialis* (Chlorophyceae)," *PLoS ONE*, Vol. 6, September 2011.

From Sensing to Enhancing Brain Processes
141529

Year 2 of 3

Principal Investigator: L. E. Matzen

Project Purpose:
In this project, we aim to improve human performance by directly influencing brain activity. Our focus is on improving memory and decreasing memory errors for decision-relevant information. When people study information, their brains produce a signal that correlates with their ability to remember that information later. This signal, called the Dm Effect, is not well understood, but it could potentially be used to predict future memory performance and thus help people avoid errors. In this project, we are using electroencephalography (EEG) to characterize the Dm Effect under different memory test conditions. In FY 2011 and FY 2012, we will test two intervention techniques that are hypothesized to improve memory performance: cognitive training and transcranial direct current stimulation (tDCS). We will use human subject experiments and dynamical systems modeling to assess and augment the effectiveness of each of these interventions. We will test their impact on both the Dm Effect and on subsequent memory performance, a paradigm that will establish causal links between recorded brain activity and task performance.

This project will create a framework for using brain activity to create focused interventions that improve human performance. We will combine cognitive training and tDCS techniques in new, targeted ways, and use EEG and computational modeling to assess their ability to optimize brain activity for specific individuals and tasks. This multifaceted approach will produce novel experimental evidence regarding the relationship between brain activity and memory performance. This information will be direct evidence that cannot be obtained from traditional correlational studies, and would represent a significant advance in the science and application of cognitive neuroscience. In addition, if the techniques employed in this project, alone or in combination, can produce substantial enhancements in memory performance, they can be applied to improving performance in individuals whose jobs involve high-consequence decision -making.

Summary of Accomplishments:
In FY 2011, we continued the analysis of the EEG data collected in FY 2010. We developed a method for modeling brain activity that is capable of predicting whether or not a participant is using an effective memory strategy. The model's predictions were confirmed by an analysis of the participants' behavioral data. The 2011 Augmented Cognition Conference accepted a conference paper on this work. This work was also presented at the Society for Applied Research in Memory and Cognition conference in June. Two additional journal publications are in preparation.

We are currently conducting one EEG study in collaboration with researchers at the University of Illinois, one tDCS study in collaboration with researchers at the Mind Research Network and Georgia Tech, and three EEG experiments at Sandia with assistance from collaborators at the Center for the Advanced Study of Language. These experiments are testing the effects on memory performance that can be attributed to working memory training, imagery strategy training, lateralized visual presentation, and stimulation of the right medial temporal lobe using tDCS. These studies are producing rich data sets that will allow us to investigate the effectiveness of cognitive training and brain stimulation for enhancing memory accuracy and reducing memory errors. These data will also allow us to continue the development of our model of brain activity and expand it to predict which individuals will receive the greatest benefit from specific memory strategies and cognitive training techniques.

Significance:
This project will advance the dynamical systems theory of brain function and provide a scientific framework for engineering innovative neurotechnologies, establishing Sandia as a leader in both of these areas. In standing up an electrophysiology laboratory at Sandia, this project creates a unique facility capable of conducting national security research that is classified or otherwise sensitive. These developments position Sandia to provide science-based technology solutions to DOE and other national security agencies with interests in enhancing human performance, training effectiveness, personnel selection, and assured readiness.

Refereed Communications:
L.E. Matzen, "Cultural Neuroscience and Individual Differences: Implications for Augmented Cognition," Lecture Notes in Artificial Intelligence, *Foundations of Augmented Cognition: Directing the Future of Adaptive Systems,* 2011.

M.J. Haass and L.E. Matzen, "Using Computational Modeling to Assess use of Cognitive Strategies," Lecture Notes in Artificial Intelligence, *Foundations of Augmented Cognition: Directing the Future of Adaptive Systems,* 2011.

L.E. Matzen, E.G. Taylor, and A.S. Benjamin, "Contributions of Familiarity and Recollection Rejection to Recognition: Evidence from the Time Course of False Recognition for Semantic and Conjunction Lures," *Memory*, vol. 19, pp. 1-16, January 2011.

Genome-Wide RNA Interference Analysis of Viral Encephalitis Pathogenesis
141530

Year 2 of 3
Principal Investigator: O. Negrete

Project Purpose:
The highly pathogenic viruses that cause encephalitis (acute inflammation of the brain) include a significant number of emerging or re-emerging viruses that are also considered potential bioweapons. Rift Valley Fever Virus (RVFV) is a prime example of such a virus that causes serious morbidity and mortality in both humans and livestock. The lack of efficient countermeasure strategies, the potential for dispersion into new regions, and the pathogenesis in humans and livestock make RVFV a serious public health concern. RVFV infects a broad host range indicating that the host requirements for virus entry and replication are widely distributed. To date, a systematic analysis of the host factors involved in RVFV infection and pathogenesis have not been described. To identify host proteins that are required for RVFV infection, we have chosen to use RNA interference (RNAi) technology, a powerful genomic approach used to investigate host factors involved in virus replication on a systems level. Furthermore, to improve the efficiency and speed of genomic screening in high-level biocontainment, we are developing a high-throughput microfluidic platform to perform genome-wide RNAi. The microfluidic device combines cellular microarray, cell transfection, and polydimethylsiloxane (PDMS)-based microfluidic channels to efficiently introduce RNAi libraries into mammalian cells within a portable and cost-effective platform. Computational network analysis will compare genome-wide molecular pathways of the attenuated RVFV-MP12 strain biosafety level (BSL-2) and the pathogenic RVFV-ZH501 strain (BSL-3) to identify key host proteins involved in viral encephalitis pathogenesis. Extension of these studies to other viral encephalitides such as Nipah virus, West Nile virus, and Venezuelan Equine Encephalitis virus, may lead to the development of novel broad- spectrum therapeutics that target common host proteins involved in viral encephalitis pathogenesis to treat these diseases for which no effective therapeutics currently exist.

Summary of Accomplishments:
During FY 2011, we conducted a genome-wide RNA interference (RNAi) screen by traditional methods. In the RNAi screen, HeLa cells were reverse transfected with a small interfering RNA (siRNA) library in a 384 well format then infected with the recombinant vaccine strain RVFV MP12 encoding green fluorescent protein (GFP). At 24 hours post infection, the cell titer and GFP fluorescence were measured from the plates to identify those genes involved in virus entry and replication. The initial screen hits were reevaluated in a secondary screen and we confirmed 597 cellular genes whose knockdown reduced viral infection by 34% or more in 5 independent plates. These 597 genes were classified into 30 different canonical pathways including endocytosis, signaling G protein coupled signaling to phospholipase C, locomotion, chemotaxis, and cell matrix adhesion. We have followed up on a novel endocytosis pathway used by Rift Valley Fever virus for cell entry and presented the results at the International Union of Microbiological Societies (IUMS) International Congress of Virology conference held September 2011. Additionally, we have developed a miniaturized high-throughput microfluidic RNAi screening platform. The microfluidic device design is based on cellular microarray technology, created on microscope slides that use chemical means to introduce small interfering RNA (siRNA) in mammalian cells. PDMS-based microchambers and channels enclose the siRNA spots thus minimizing reagent consumption, numbers of cells used per experiment, and preventing contamination issues observed in open systems. RNAi transfection of siRNA against GFP has shown specific inhibition of infection with RVFV MP12 encoding GFP. In our results, we have shown 75% knockdown efficiency in the microfluidic device, which mirrors results we have observed on the benchtop screen. These results

will be presented at the Miniaturized Systems for Chemistry and Life Sciences conference in October 2011.

Significance:
This project benefits the DOE scientific and defense and DHS awareness and response strategic goals by providing an understanding of the mechanisms by which biodefense viral pathogens cause lethal encephalitis disease. We will employ Sandia's microfluidic technology to BSL3/4 labs in need of small footprint and highly automated devices that improve the speed at which host genes and pathways involved in viral infection are identified, thus supporting therapeutic development to combat infection.

Neurological Simulations for Emerging Brain Maps
141531

Year 2 of 3
Principal Investigator: R. Schiek

Project Purpose:
Advances in imaging and reconstruction technologies are driving many research projects to map all of the neurons in some small animal brains. While these projects will produce detailed topology of their targeted subjects, the ability to then simulate in detail the neural physiology is limited to high-fidelity simulations of a few neurons, or lower-fidelity simulations of thousands of neurons (i.e., multi-compartment neuron models versus behavioral, integrate-and-fire neuron models). Sandia's parallel circuit simulator, Xyce, can address large scale neuron simulations in a new way by greatly extending the range within which one can perform high-fidelity, multi-compartment neuron simulations. Additionally, the network simulation framework provided by Xyce can be used to migrate high-level, cognitive models to a high-performance computing platform. To be successful, this work must engage the neuroscience community and researchers developing the brain maps by providing access to Xyce and demonstrating that Xyce can tackle complex problems. Since the topology of a neural system is more highly linked than a circuit, improved preconditioning and new solver technologies may also be needed as well as new computational tools (i.e., reduced-order modeling and adjoint sensitivity). Programmatically, this project will connect the cognitive science work at Sandia to the high-performance computing community and provide context for further engagement between Sandia and the neuroscience simulation community.

This work casts neurological simulation in a new mathematical formulation that is commonly used in electrical circuit simulation. Such a reformulation allows the use of advanced mathematical techniques to improve on the state of the art in: parallel simulation performance, model order reduction, multiscale coupling, uncertainty quantification, and global system analysis. There is risk that any of these potential advantages will not evolve to be better than the current state of the art. However, advances in any one of these fields will advance neuron simulation science.

Summary of Accomplishments:
A key challenge to this work from its start was to address multiple levels of abstraction in neuron modeling within this one simulation framework. While the analogy and connection between fine-scale, compartmental neuron modeling and electrical simulation is straightforward, it was less obvious how to efficiently work at higher levels of abstraction. This year, by working with our collaborators Howard Eichenbaum, Neal Cohen, and student Patrick Watson, we have identified and started to implement population-level models that can be used in studies of neurogenesis and plasticity in learning and memory. This population modeling is significant for two reasons. First, it can still couple to detailed neuron models, allowing one to study systems at multiple levels of fidelity. Second, the population-level model allows for rapid changes in neuron number and connectivity, which are system level changes difficult to fit within the sparse matrix structure of a network, ordinary differential equation solver.

A second key development this year is the scaling studies of neuron systems with high levels of synaptic connectivity. Anatomical studies have found that a single neuron may be connected to 1,000 or 10,000s of synapses. This high level of connectivity could pose significant problems in the parallel partitioning and preconditioning of the problem for simulation. While the work is still developing, we have studied systems with 10, 50 and 100 synapses per neuron and have found good scaling up to 64 processors. Significantly, it was found that when running the same type of simulations, the code NEURON took about 10 times the number of time steps to complete a simulation and remain stable. Thus, this work is demonstrating that is can improve over the existing state of the art.

Finally, new results will be presented at the Design Automation Conference and the Society for Neurology meeting.

Significance:
A fundamental unknown of neurological functions is the level or scale at which various cognitive function occurs, such as pattern recognition and completion. Allowing the construction of neuron system simulations at multiple scales enables a researcher to study functional separation of the scales and how a brain might function. Related to this is the second significant result in that neural systems at any scale can be densely connected and very large. By demonstrating that existing techniques in parallel partitioning can significantly improve the simulation efficiency, this work enables researchers to focus on the neurology and not the problem implementation.

Real-Time Neuronal Current Imaging of the Human Brain to Improve Understanding of Decision-Making Processes
141532

Year 2 of 3
Principal Investigator: H. D. Jones

Project Purpose:
Understanding cognitive processes that underlie decision-making will enable Sandia to determine variables that impact the ability to make optimal decisions under stress and uncertainty — situations regularly encountered in national security domains. A major limitation in understanding the neuronal basis of decision -making is the lack of imaging technologies capable of directly measuring neuronal responses to cognitive challenges with high temporal and spatial resolution.

Magnetoencephalography (MEG) and electroencephalography (EEG) have impressive temporal resolution (millisecond), but are limited in their ability to localize the neuronal signal. In contrast, functional magnetic resonance imaging (fMRI) has high spatial resolution (millimeter), but poor temporal resolution due to its dependence on the temporally sluggish vascular response. Moreover, measurement of hemodynamic rather than electrical signals renders functional magnetic resonance imaging (fMRI) an indirect measurement of neuronal activity.

This project will use proton magnetic resonance spectroscopy (^{1}HMRS) to directly detect neuronal responses during perceptual decision-making by investigating the effects of synchronously firing cortical neurons (and their associated magnetic fields) on the water proton signal. These event-related magnetic fields (ERFs) are the neuronal currents fields that would be detected by MEG. However, by detecting them with an MR-based method, the sources of the fields can be precisely located and a true neuronal current imaging method can be devised. The ERF's effect on the ^{1}HMRS signal is expected to be weak and hampered by scanner and physiologic noise. Sandia's demonstrated area of expertise in signal processing and multivariate data analysis of spectral image data will be applied to the ^{1}HMRS data to improve the sensitivity to small neuronal responses during decision-making events. This novel approach is intended to provide brain researchers with a new and powerful functional brain imaging capability that will have unprecedented spatial and temporal resolution and can ultimately be used to improve our understanding of decision-making.

Summary of Accomplishments:
An ^{1}HMRS neuronal current (NC) study designed to avoid interfering blood oxygen level dependent (BOLD) responses was completed and analyzed. The visual cortex (VC) was imaged using 10 subjects during a decision-making task that included white-black or red-black checkerboard visual stimulation 40 ms after the initiation of the free induction decay (FID). For control, the rostral anterior cingulate cortex (rACC) was imaged using 10 subjects with the same visual stimulation. Both ANOVA (analysis of variance) and multivariate curve resolution (MCR) analyses demonstrated positive results for detection of NC in the VC but not in the rACC control region. Both analyses showed a shift in the T2* ^{1}HMRS signal in the VC with visual stimulus but not for the rACC control. Unfortunately, the rACC T2* signal is more erratic than that from the VC, and a startle in response to the stimulus could not be excluded as a source of the apparent NC signal.

Therefore, a second study was designed to mitigate the above problems while simultaneously making the measurement in the presence of BOLD as required for future NC imaging experiments. In this experiment, we implemented efficient background correction, two stimulus delays within a given subject, and auditory stimulus controls, while simultaneously attempting to saturate the BOLD. All FIDs were collected in the VC with either the same checkerboard visual stimulations as before or with auditory stimulations. Each stimulus was presented with either a 20 or 50 ms delay time since these are optimal for differential detection. The two delay times are necessary to confirm that differences between auditory and visual stimuli can be definitively attributed to NC since the NC signature should vary in location and size with the two delays. This experiment has recently been completed and initial results are encouraging; for example, we are observing the signal from the visual stimulus but not the auditory stimulus.

Significance:

Understanding the factors in the brain that affect the performance of human decision-making under stress and uncertainty is important to the national security mission of Sandia and other federal agencies such as DoD and DHS. The development of neuronal current imaging techniques and equipment capable of directly measuring the neuronal current in the human brain with both high spatial and temporal resolution would help provide researchers with a new tool in this understanding.

Diffusion Among Cognitively Complex Agents in Limited Resource Settings
148898

Year 2 of 3
Principal Investigator: K. Lakkaraju

Project Purpose:
The S&T objective of this work is to study diffusion of information in complex settings (i.e., ones that exhibit socially complex agents (differing numbers of neighbors, captured through a social network); cognitively complex agents (continuous, interdependent belief structures that change over time, rather than binary, independent belief structure, captured through a cognitive network); and limited resources (bounded rationality, modeled by limiting the resources for communicating and integrating information). Current diffusion models focus on social structure, leaving cognitive structure simple. We propose to develop a novel model of diffusion that exhibits these three factors.

This is a high-risk project because, to our knowledge, no one else has developed a model with complex cognitive agents. The project has high potential because understanding the factors that influence the speed of diffusion is important in numerous areas of federal agency priorities. The hypothesis of this project is that diffusion will increase in speed as a function of an increase in the connectivity of the social network, and a decrease in the connectivity of the cognitive networks of individual agents. We propose to test this hypothesis by developing a model of diffusion, implementing the model in a simulation framework, and then measuring the speed of diffusion (number of interactions) as we vary the connectivity of the cognitive and social networks. The intention of this project is to develop a model that will allow one to ask basic research questions about the interaction between cognitive networks and social network structure.

Summary of Accomplishments:
Significant technical progress has been made towards the milestones for model implementation and investigating the model over a wide range of parameters.

- Development of a model of attitude change incorporating positive/negative information: captures bidirectional reasoning where conclusion impacts evidence assessment.
- Evaluation of attitude change model and establishing its dynamics as being similar to known attitude change results.
- Preliminary evaluation of the impact of cognitive effort on attitudinal change.
- Investigating impact of community structured graphs on attitudinal change.

Presentations/Publications:
Presentations at 3 conferences:

- Association for the Advancement of Artificial Intelligence (AAAI) Fall Symposium on Complex Adaptive Systems
- Human Social Cultural Behavioral Focus Meeting 2011
- IEEE Homeland Security and Technologies Conference

Publications:
-- (In review) Book chapter on selected paper from AAAI Complex Adaptive Systems (CAS) symposia.
-- Lakkaraju, K. and A. Speed, AAAI Fall Symposium on Complex Adaptive Systems, "Population Wide Attitude Diffusion in Community Structured Graphs," 20ll.

Significance:
DOE will benefit because we can model the diffusion of climate change information. In addition, the diffusion of TTPs (such as IED tactics) is important for DOE's mission of protecting the labs, as well as helping the DoD understand capability evolution between theatres of operation. DHS will benefit from understanding the diffusion of critical safety information that could impact the resiliency of a community.

Ultrasensitive, Amplification-Free Assays for Detecting Pathogens
149705

Year 2 of 3
Principal Investigator: R. Meagher

Project Purpose:
Quantitative analysis of nucleic acids (DNA or ribonucleic acid [RNA]) is a powerful approach for detecting and identifying pathogens, including potential bioweapons and pandemic threats. All current approaches for nucleic acid detection, short of direct sequencing (e.g., microarrays, PCR, blots), rely upon hybridization of nucleic acid primers or probes to a specific target sequence. Most assay formats require enzymatic amplification such as polymerase chain reaction (PCR) to generate a high enough concentration of nucleic acid for detection. PCR-based methodologies are sensitive and powerful, but require a well-equipped lab with cold storage and clean samples — enzymatic approaches are sensitive to contaminants and inhibitors in environmental samples.

Rather than using PCR to generate 10^8 or more copies of a template in a ~100 µL reaction volume, we propose to confine the total nucleic acid content of a sample into a volume of ~100 pL adjacent to a nanoporous polymer membrane (roughly 10^6-fold increase in concentration). The total contents of the concentrated sample volume can be directly analyzed by microchannel electrophoresis, with minimal dilution of the sample plug. A simple detector with ~100 pM sensitivity could thus detect hybridization of ~6,000 target molecules, which corresponds roughly to the number of ribosomal RNA molecules in a single bacterial cell.

This project entails a proof-of-concept study, including experimental demonstrations of the assay with model bacterial and viral targets, coupled with analytical and computational modeling of the underlying transport and kinetic processes. Transport modeling will provide an estimate of the maximum rate of nucleic acid concentration, and concentration profiles of multiple ionic species involved in hybridization, which will be used to develop a kinetic model for hybridization. The resulting theoretical estimates of assay performance will be used to benchmark our experimental investigations, enabling us to optimize parameters such as membrane chemistry, buffer systems, electric field, and temperature cycling.

Summary of Accomplishments:
In the second fiscal year of the project, we have further characterized the process of electrophoretic concentration of nucleic acids at photopatterned polyacrylamide membranes, and optimized procedures for electrophoretic separation following concentration. To summarize: negatively charged membranes (incorporating 100 mM acrylic acid along with polyacrylamide/bisacrylamide) offer increased rate of concentration by allowing higher electric fields to be used and more complete exclusion of nucleic acids, although strong concentration polarization of ions diminishes the efficiency of the subsequent size-based separation. This can be mitigated by an additional "pre-run" following the preconcentration, during which excess ions are swept down the separation channel prior to injection of sample. Even with this procedure, preconcentrations beyond about 10 minutes do not significantly improve signal-to-noise ratio. In contrast, uncharged membranes are permeable to smaller DNA at lower electric field strengths, and require several runs of "conditioning" prior to performing well, perhaps due to entrapment of DNA leading to a buildup of a low level of fixed charge. Once "conditioned," the uncharged membranes yield a cleaner, more consistent separation, but require longer to achieve similar concentration factors due to the necessity of lower voltage to prevent DNA penetration into the membrane.

Experimental data has been compared to existing models of analyte concentration at microchannel-nanochannel interfaces. Due to the very low electroosmotic flow present in the current system, operation is in a regime characterized by previous researchers as follows: buffer ions experience strong concentration polarization which propagates rapidly away from the membrane, whereas analytes (i.e., DNA) are stacked at the membrane interface. Using reasonable estimates for charge density within the 100 mM acrylic acid membrane suggest buffer ion concentrations near the membrane approach 10–20 times the "background" concentration, which is consistent with observations of degraded separation performance following long preconcentrations.

Significance:
Biological warfare agents and infectious diseases present a real threat to homeland security and public health. Existing assays for these agents range from highly rapid but nonspecific, to very specific but slow and complex. The proposed research will introduce molecular specificity into the space of rapid assays for biological threats. The assay could also serve as a useful research tool for detecting and quantifying nucleic acids in a wide variety of research contexts. This ties to DHS and DOE science missions.

Apart from the intent of the project for amplification-free hybridization assays, the technology developed to date could be useful as a preconcentration step to improve detection limits for any sort of DNA analysis. For example, the ability to separate and detect DNA at starting concentrations of 1 pM or less would be useful for detection of DNA after just a few cycles of PCR, which is an important analysis, for example, in library preparation for DNA sequencing. The preconcentration and separation thus has potential for ongoing research initiatives on its own merits, apart from the hybridization assay.

An Adaptive Approach to Modeling Human Reasoning
150966

Year 2 of 3
Principal Investigator: D. J. Stracuzzi

Project Purpose:
This research aims at exploring the notion that a combination of computational reasoning techniques is required to emulate the powerful and pragmatic nature of human reasoning. A key goal will be to identify and incorporate psychologically plausible computational mechanisms for guiding the reasoning process. The project will address questions about how to represent knowledge, combine computational reasoning techniques, and incorporate the effects of learning and experience on reasoning in psychologically plausible ways. Our approach of combining multiple reasoning techniques and using learning as a guide distinguishes the proposed work from past efforts at computational reasoning, which tend to focus on a single technique and ignore the question of how to decide which method to use in a given situation. The proposed work is both high risk, due to the novelty of the effort, and high -impact, due to the potentially broad applicability of the results. If successful, this work will provide a foundation for future research on human decision-making, automatic knowledge base acquisition, fusion of low-level state descriptions into high-level, actionable knowledge, and neurally plausible models of high-level reasoning mechanisms. Potential applications include collaborative human-computer approaches to cyber security and satellite data analysis, and realistic reasoning and decision-making capabilities for autonomous agents used in training software.

Summary of Accomplishments:
Scientific and technical achievements so far include development of a mathematical framework for combined logical and statistical reasoning, along with incorporation of several well-known psychological biases. Key lessons learned surround the development of the underlying knowledge representation, which now supports both the computational and psychological aspects of the system quite naturally. Specifically, we discovered a graph-like representation that emulates many useful properties of hypothesized psychological structures. Other accomplishments include a smooth integration of logical and statistical information into the system, such that the algorithms required for processing the information execute in an online manner and require minimal computation. To date, work from the project has been accepted to two conferences, one in the form of a paper and poster presentation, the other in the form of an oral presentation.

Significance:
Understanding and emulating human reasoning plays a key role in developing technologies that both aid humans in their work and monitor for errors or malicious acts. The integrated approach to reasoning and learning taken by this project has clear implications for applied research in both cyber security and satellite data processing. Both of these mission-relevant areas suffer from the same problem: the volume of data streaming in from sensors (information networks and satellite images) is quickly outpacing the processing capabilities of human analysts. The tight integration of reasoning and learning implies that a system based on this work could be used to construct a model of knowledge and decision-making in the human analysts, and then apply that model to the incoming data to help reduce the load placed on humans. The relatively low processing costs associated with our algorithms also means that such a system could filter larger quantities of data using less computational resources than other methods. Finally, the combination of logical, statistical, and psychologically plausible reasoning techniques substantially increases the ability of such a system to collaborate directly with human analysts by explaining its decisions and processing complex feedback provided by human users.

With respect to the broader S&T community, the combination of logical and statistical inference capabilities with learning represents a meaningful step forward on well-studied problems. The techniques developed in this project can serve as an improved foundation for a variety of research in areas such as intelligent agents, cognitive architectures, and common sense reasoning, as well as a possible modeling tool or point-of-comparison for research into human reasoning.

Refereed Communications:

D.J. Stracuzzi, "A Plausibility-Based Approach to Incremental Inference," to be presented at the *Association for the Advancement of Artificial Intelligence Fall Symposium on Advances in Cognitive Systems*, November 2011.

From Neurons to Algorithms
151345

Year 1 of 3
Principal Investigator: F. Rothganger

Project Purpose:
A mechanistic description of how the human mind works requires demonstrating links between brain mechanisms and behavior across a wide range of scales: molecular, cellular (neurons), neural circuits, brain regions, and cognitive function of the whole brain. Each of these is best expressed with its own set of abstractions and tools. We focus on the mapping between neural circuits and the functions they implement.

We hypothesize that the interactions between neural components implement functions in the brain that can be sufficiently described in terms of signal processing and information transformations, that is, algorithms. If this hypothesis is correct, then it enables us to apply a set of well-developed theoretical tools, and indicates a systematic method to assemble structural information into functional models of the brain.

We propose to express both algorithms and neural structures in the form of difference equations relating their constituent variables. These models can also be visualized by translating them into circuit diagrams. While difference equations can represent fine details in each of these separate domains, they can also represent both domains at a high level in effectively the same form. Consequently, they provide a framework within which we can move between levels of analysis as needed, and also comprehend the function of the system as a whole.

The task of describing the function of neural circuits has proven quite difficult for the field as a whole. Algorithms have been proposed for this purpose, but in each case we have examined, these models contain elements that lack physiological support. On the other hand, models built strictly bottom up from the physiology are not quite functional as algorithms. The proposed approach bridges this gap by representing both sets of work in a common form that allows them to be easily compared and combined to discover new models.

Summary of Accomplishments:
The first phase of this project had two key goals:
1. Develop software tools that enable us to collect and represent neural structure. A key requirement for this software is that the contents be computable, in the sense that it forms a concrete mathematical model of the system in question and that it can be output automatically to a simulation system such as Xyce that operates on high-performance computer (HPC) systems.
2. Add a neuroscientist to the team who will lead the selection of neural structure data to input to the database.

Results:
1. The software tools, while still evolving, have been tested end to end on the Hodgkin-Huxley model. This includes a simulation run on Sandia’s Red Sky high-performance computer.
2. A neuroscience post doc will be joining us in late October 2011. In addition, we have formalized a collaboration agreement with Dr. Mark Gluck (Rutgers University), a leading neuroscientist.

Significance:

A long-term goal, beyond the scope of this project, is to represent the computational structures of the brain in a compact generative form. This could form a concise description of cognition itself. Our work on representing connectomic data and automatically generating neural simulations from them is a step in that direction.

Human behavior is a direct result of neural functioning. The proposed neural modeling work is part of ongoing research and development of technology around the “human element.” The human element impacts most NNSA mission areas. In many cases, this involves a human's ability to understand and act in uncertain, yet time critical, situations with nationally significant consequences. Impacts of cognitive research include NNSA's adaptivity to emerging threats, Nuclear Weapon (NW) surveillance, NW Information Enterprise (including NWie), physical security, design basis threat, use control, knowledge preservation, insider threat surveillance, field intelligence, workforce utilization, and economic issues associated with global climate change.

Incremental Learning for Automated Knowledge Capture
151346

Year 1 of 3
Principal Investigator: Z. O. Benz

Project Purpose:
People responding to high-consequence national-security situations need tools to help them make the right decision quickly. The dynamic, time-critical, and ever-changing nature of these situations, especially those involving an adversary, requires models of decision support that can dynamically react as a situation unfolds and changes. Automated knowledge capture is a key part of creating individualized models of decision -making in many situations because it has been demonstrated as a very robust way to populate computational models of cognition. However, existing automated knowledge capture techniques only populate a knowledge model with data prior to its use, after which the knowledge model is static and unchanging. In contrast, humans, including our national-security adversaries, continually learn, adapt, and create new knowledge as they make decisions and witness their effect. This artificial dichotomy between creation and use exists because the majority of automated knowledge capture techniques are based on traditional batch machine-learning and statistical algorithms. These algorithms are primarily designed to optimize the accuracy of their predictions and only secondarily, if at all, concerned with issues such as speed, memory use, or ability to be incrementally updated. Thus, when new data arrives, batch algorithms used for automated knowledge capture currently require significant recomputation, frequently from scratch, which makes them ill suited for use in dynamic, time-critical, high-consequence decision making environments.

We propose to research novel incremental learning algorithms that are suitable for automated knowledge capture for computational cognitive models in dynamic, real-time settings. Our approach is to study the interplay between learning and memory from a computational perspective incorporating psychological insights. Our goal is to break down the artificial division between the processes of automated knowledge capture and model execution by having knowledge capture occur continuously while the model is executing. This provides the potential for models with more human-like behavior for high-consequence decision-making by continually adapting to change and improving.

Summary of Accomplishments:
In the first year of this project, we have accomplished the primary goal of establishing a benchmark for existing incremental learning algorithms. To do this, we developed novel ways of measuring and comparing batch and incremental algorithms by developing experimental procedures that mimic typical contexts in which incremental algorithms are used for automated knowledge capture. We implemented a software harness for comparing algorithms using a wide variety of datasets and evaluation metrics. As part of this harness, we created a capability to handle a wide variety of datasets in different data formats. Within this harness, we implemented a large suite of classic and contemporary incremental learning algorithms for categorization and benchmarked them on several real-world datasets. In doing so, we have demonstrated strong performance for certain incremental algorithms on some of these datasets. We have also discovered gaps in the existing research on incremental algorithms, such as lack of understanding of how well incremental algorithms generalize across domains, lack of work in combining incremental supervised and unsupervised algorithms, lack of learning theory for handling changes in data distribution, and that most evaluation approaches do not match real-world usages. We have attempted to address some of these gaps in our benchmarking approach and plan on addressing more in future work.

In addition, we:

- Created a large suite of incremental learning algorithms.
- Designed novel ways of measuring and comparing batch and incremental algorithms
- Demonstrated strong performance of incremental algorithms on real-world datasets.
- Wrote a paper in submission to *Journal of Machine Learning Research*.
- Created a data-processing pipeline for dealing with arbitrary datasets.
- Fostered implementation of LDRD project findings for work in the NW domain and high-visibility projects in 5600/DSA.
- Established benchmark for classic and contemporary incremental categorization algorithms.
- Established a community of interest across the lab in incremental learning algorithms.

Significance:
This project supports the national security missions of DOE, DoD and DHS by providing science and technology in support of the human element that is critical to many mission areas. It addresses a fundamental barrier to using computational models of cognition by updating models with relevant knowledge in a timely manner to support a human's ability to understand and act in urgent and uncertain situations with nationally significant consequences. This will also increase their applicability to environments, such as physical and cyber security that involve adversaries who constantly adapt tactics and strategies by also enabling the models to adapt.

A Comprehensive Approach to Decipher Biological Computation to Achieve Next Generation High-Performance Exascale Computing
151347

Year 1 of 3
Principal Investigator: C. D. James

Project Purpose:
The human brain (volume=1200 cm^3) consumes 20 W to perform >10^{16} operations/s. Current supercomputer technology has reached 10^{15} operations/s, yet it requires 1500m^3 and 3 MW, giving the brain a 10^{12} advantage in operations/s/W/cm^3. Thus, to surpass exascale computation (10^{18} operations/s) with reasonable power and volume, two achievements are required: 1) improved understanding of computation in biological tissue, and 2) a paradigm shift towards "neuromorphic" computing where hardware circuits are given architectures that mimic neural tissue. To address 1), we will interrogate corticostriatal networks in rat brain tissue slices. These networks are crucial to processing massive amounts of information (sensory, motor, reward, cognitive inputs) during decision making, thus our objective is to identify key information processing elements that enable the collection and synthesis of such information into actionable decisions. Elements that will be quantitatively measured include signal thresholding and spike-timing and frequency-dependent changes in synaptic connections. To address 2), we will instantiate biological computing elements found in 1) into a microfabricated neuromorphic hardware circuit with demonstrated capability for low-power analog-like decision-making. Complementary metal-oxide-semiconductor (CMOS) transistors will be assembled into "neurons" and memristors (nanoscale structures capable of storing information) will serve as "synapses." We will develop novel strategies to regulate memristor state using adjacent charge-carrier storage sites to mimic the molecular regulation of biological synapses. The potential of neuromorphic systems for high-performance low-power computing will be demonstrated with a circuit that can engage in simple "decision-making", such as the recognition of trained stimulation patterns under adverse conditions (incomplete or confounding input).

This project is innovative in its characterization of biological computing in neural circuits involved in decision-making, and in the implementation of similar computing strategies into silicon hardware. It will generate science knowledge in biological computing and nanoscale science while generating a silicon hardware deliverable.

Summary of Accomplishments:
We have measured and assessed the frequency characteristics of plasticity in mouse corticostriatal networks. Initially, we have focused on high frequency (100 Hz) and low frequency (10 Hz) stimuli to assess the endpoints of the frequency range with future frequencies chosen based on this data. We have also varied the amplitude of the stimuli to assess the effects of the stimuli magnitude on the development plasticity. Currently, we have 55 individual experiments conducted with various stimulation paradigms. We wrote custom MatLab scripts for the data analysis that allows raw population spike data to be processed into measurements of synaptic plasticity.

Another accomplishment was the assembly of an optical stimulation and recording setup for dissociated neurons plated and grown on coverslips. We are using an infrared femtosecond laser to optically excite neurons to fire action potentials. When combined with a spatial light modulator, we will be able to generate complex multi-point stimuli to large complicated neural networks in order to assess the mechanism by which living networks process large amounts of input data. Currently, we have written custom MatLab scripts to analyze image data of living neurons to quantitatively measure fluorescence intensity (which correlates to calcium flux) in cell bodies and thin axonal and dendritic processes.

Finally, we have begun designing and fabricating alternative memory structures including resistive and multiferroic memory. We are currently fabricating bismuth manganate multiferroic structures with sidewall microelectrodes to measure the magnetic and electric properties of these films without a dominant fringing field component.

Significance:
This project will further DOE's mission of advancing the field of scientific computing, including the development of a new nanotechnology-enabled biologically inspired computing strategy. This work has the potential to create a paradigm-shift in computation, and enable exascale computing with dramatic reductions in power consumption and hardware volume. This will improve our ability to tackle 21st century multiphysics computational problems such as nuclear stockpile surety, weapon detonations, energy harvesting/storage/distribution, and predictive models of infectious disease pandemics.

The resistive memory devices also have potential application due to their radiation-hardened properties. Resistive memory is also being investigated for special properties with regard to secure electronics applications. A final interest for these resistive memory devices is in the development of neuromorphic-type computing architectures that are capable of fast and highly precise pattern recognition. This type of application would be useful in covert satellite imaging efforts.

On the biological network portion of the project, our analysis of the frequency characteristics of corticostriatal networks will result in novel data because these networks are not well characterized in the available literature. Our use of various input stimuli configurations (amplitude, frequency, and integrated amount of current injected) will lead to some clarification with regard to synaptic plasticity in these networks and will lead to a high impact journal publication.

Systems Biology in 3D: Monitoring and Modeling the Dynamics of *Francisella tularensis*-associated Granuloma Formation
151348

Year 1 of 3
Principal Investigator: E. May

Project Purpose:
Formation of granulomatous-necrotic lesions in mice infected with the intracellular parasite, *Francisella tularensis* (Ft), a category A bioterrorism agent, may serve to control and regulate early stages of infection. Traditional sample-sacrifice experimental protocols have enabled significant insight into the cellular composition of these granulomas; however, an understanding of multiscale mechanisms and host-pathogen interactions that mediate Ft-related granuloma formation is lacking. Specifically, we propose to explore: 1) the functional role of macrophages and effector molecules (e.g., nitric oxide [NO]) in formation and establishment of an unfavorable granulomatous-microenvironment and 2) the intracellular response of *Francisella tularensis* (Ft) within the granuloma-associated microenvironment

Existing experimental methods do not capture the dynamics of host-pathogen intra/intercellular events that lead to 3D granulomatous structures, thereby preventing full exploration of the role of these structures on immunopathogenic outcomes of Ft. Using a multidimensional systems-biology approach, we will investigate the correlation between intracellular-scale events (e.g., chemokine-mediated cell recruitment, NO biosynthesis) and granuloma formation. Further, we will explore the impact of granulomatous structures on Ft viability and dissemination during infection. We will develop an experimental platform to enable real-time dynamic profiling of Ft infections of host mononuclear cells in a three-dimensional environment. The platform will consist of a 3D microfluidic porous collagen-based scaffold that will serve as a synthetic extracellular matrix (ECM) for interrogating host cell responses to pathogen exposure in an ex vivo microenvironment. This platform will enable real-time optical and electrochemical monitoring of Ft-infection and granuloma formation events. Quantitative and semi-quantitative spatio-temporal observations will be used to develop a theoretical model of this important host response mechanism, which will enable us to explore and develop new hypotheses regarding the kinetics of host-mediated granulomatous structure and their protective function during Ft infection.

Summary of Accomplishments:
Our goals and technical accomplishments include the following:
Goal 1: Investigate and characterize the effects of host-mediated microenvironment stress on Ft persistence

- We cultured Ft under normal growth conditions, collected intracellular extracts, and extracellular supernatant to quantify relative concentrations of metabolites over time.
- Using murine macrophage-like cell lines (RAW cells), we cultured cells under non/interferon (IFN)g-stimulatory conditions and collected intracellular extracts for metabolomics analysis.
- Nuclear magnetic resonance (NMR)-based metabolomic profiling of samples were completed and are being repeated using various extraction protocols to determine optimal method that can resolve substrates of interest.
- Using RAW cells and quantum dots, we prepared samples for preliminary uPIXIE (Proton-Induced x-ray Emission) analysis, a method that can provide subcellular resolution imaging of metals.

Goal 2: Experimental platform for multiscale, dynamic profiling of Ft-granuloma formation and function

- We are using the MicroCoRD platform to study and quantify cellular movement in response to chemokine/cytokine gradients created by an activated or infected cell.
- We have characterized the viability of human embryonic kidney (HEK) and RAW cells grown on carbon scaffold with and without synthetic extracellular matrix substrate. Using an antibody-based detection system, we have analyzed cytokine and chemokine production of stimulated/non-stimulated cells during growth on carbon/ extracellular matrix (ECM) substrate. Initial results suggest comparable growth and response for growth on carbon and carbon/ ECM.
- We have developed and tested a modified microfluidic chamber to enable uPIXIE analysis of samples. These chambers are being used for our initial samples.

Goal 3: Multiscale theoretical modeling platform for analysis and hypothesis generation

- We have developed a model of key Ft intracellular pathways (glycolysis + pyruvate metabolism, triCarboxylic Acid (TCA), pentose phosphate pathway (PPP), and nicotinamide adenine dinucleotide (NAD) biosynthesis) using publically available data and the MatLab environment. We are migrating the models to BioXyce and interfacing with Dakota for parameter fitting/optimization and sensitivity analysis.
- Using SPPARKS, we developed initial cellular models based on the Potts model for tumor growth.

Significance:

The goal of this work is to understand the role of the granulomatous structures in *F. tularensis* infection, a category A bioterrorism agent. Results will contribute to efforts to understand whether Ft-granuloma formation is simply an effective host defense mechanism or, as in Mtb-granulomas, Ft can potentially adapt to the changing microenvironment enabling the pathogen to hide within these structures, thereby evading complete elimination by the host. This can provide insight of significant relevance to DOE and national security missions with regard to biodefense.

Reverse Engineering the Host-Virus Interaction Using an Artificial Host Cell
151349

Year 1 of 3
Principal Investigator: J. C. Stachowiak

Project Purpose:
Pathogenic viruses are a primary threat to national security. Strategies for detection and therapy will benefit greatly from fundamental understanding of the mechanisms pathogens use to invade host cells. While much has been learned about the biochemistry of pathogen invasion from studying interactions with host cells, the complexity of cellular processes makes it difficult to isolate the fundamental requirements of infection, complicating design of countermeasures. For example, enveloped viruses are known to attach to receptors on the host cell surface creating the close proximity required for protein-mediated fusion of the host and viral membranes. However, the role of receptor clustering, lipid composition, and membrane deformability in viral entry remains unknown. Cells respond to pathogens with distinct biochemical patterns that are the essential targets for effective detection and defense. However, the complexity of cellular pathways makes it difficult to discover the fundamental requirements of infection. Enveloped viruses enter cells by fusing their lipid membrane to a host membrane.

These properties cannot be independently altered in live cell studies, making it impossible for conventional approaches to identify the set of necessary and sufficient conditions for viral entry, the key parameters for effective defense. Our approach is to build synthetic membrane systems with known biochemical parts (lipids, proteins) in order to learn the basic requirements of viral membrane fusion. To complement top-down studies on live host cells, we propose to construct an artificial host cell, a minimal, bottom-up environment for investigating host-pathogen interactions. An artificial cell will detect pathogen invasion by recreating the essential early events of infection by enveloped viruses (Influenza, Nipah) — entry and the start of replication. Specifically, the artificial host will consist of a lipid vesicle that contains a protein expression system and has a proscribed membrane composition (lipids, cholesterol, candidate viral receptors). We will vary membrane composition iteratively until fusion between the lipid membranes of the virus and the artificial host occurs, triggering fluorescent assays at the membrane surface and releasing viral ribonucleic acid (RNA) into the host that enable expression of fluorescent reporters. These cell-like assays will address a key question in viral entry: what are the minimal cell surface markers and physical properties of host cells that viruses require to initiate productive infection? If successful, this nontraditional study will enable a novel approach to the study of host-pathogen interactions.

Summary of Accomplishments:
Our first year has focused on developing necessary tools to access fusion between synthetic lipid membranes and the membranes of enveloped viruses. These tools include: synthetic membranes with fusogenic compositions, virus particles incorporating fluorescent reporters, and fluorescence-based assays that report fusion and allow us to examine the density and distribution of protein receptors on membrane surfaces. Our initial studies have used Vesicular Stomatitis Virus (VSV) as a model. Using synthetic lipid membranes with a fusogenic membrane composition suggested in the literature, we have developed two fluorescence-based assays of virus-membrane fusion: a bulk assay for fusion with small vesicles, and an image-based assay for fusion with cell-sized vesicles. Notably, these assays have revealed the dependence of fusion on membrane phase boundaries, a finding we will publish. In preparation for studies on Nipah virus (NiV) fusion, we have begun to incorporate the NiV cell-surface

receptor, EphrinB2, into synthetic lipid membranes. For this work, we have developed fluorescence assays that allow us to directly measure the density of protein receptors on synthetic membrane surfaces. In developing this assay, we discovered that high protein surface density leads directly to membrane bending by proteins known to participate in endocytosis. We have received excellent feedback on this work from leading peer investigators, including an invitation to speak at the Gordon Research Conference on Molecular Membrane Biology. We will submit our manuscript on this work to the journal, *Science*, and prepare external proposals for continued work. Since our model viruses are thought to fuse with curved endosomal membranes in vivo, we will use these tools in year two to build curved membrane substrates for fusion assays and to measure the density of EphrinB2 on model membranes. In summary, tools and initial findings developed in year one will enable focused examination of viral entry mechanisms in year two — dissecting specific biochemical and biophysical effects that enable membrane fusion.

Significance:
This project is relevant to several DOE missions: 1) basic understanding of host-pathogen interactions is critical to national security, 2) cell-like synthetic devices developed for basic science objectives of this project can also serve as novel platforms for sensors and therapeutics to combat bioterrorism, 3) cell-like devices provide an environment for integration of nanoscale materials with biological components to create functional nano-bio systems for DOE missions in materials science.

Biomimetic Lung Toxicity Screening Platform (bioMIMIC)
151350

Year 1 of 3
Principal Investigator: A. Hatch

Project Purpose:
While the use of engineered nanomaterials continues to burgeon, questions relating to potentially harmful human health effects linked to nanomaterial exposure have not been convincingly addressed. While animal models are considered the gold standard for physiological insight into nanomaterial toxicity, they are not feasible as first-line screening tools due to high study costs and potential interspecies variability. Conversely, single-phenotype Petri dish studies can provide cellular level toxicity readouts in a scalable manner, but seldom represent integrated tissue level physiological responses. To overcome these deficiencies, the National Research Council's report entitled *Toxicity Testing in the 21st Century: a Vision and a Strategy* (http://www.nap.edu) has identified a critical need for scalable, physiologically relevant in vitro tissue mimics that can minimize or replace animal toxicity studies while providing insight into the human effects of nanomaterial exposure.

We will develop a multicellular, 3D tissue mimic (bioMIMIC) that will significantly improve pulmonary nanotoxicology screening. Our platform will transcend the capabilities of conventional Petri-dish-based toxicity assays and provide access to the integrated tissue and system level toxicity responses that only animal/human exposure studies currently capture (e.g., coupled cytotoxicity, inflammation, nanoparticle translocation). Our unique and scalable platform will be used to assess integrated pulmonary toxicity responses induced by exposure to metal oxide nanoparticles that have been shown to cause deleterious pulmonary responses. bioMIMIC is enabled by our multidisciplinary team from Sandia, Lovelace Respiratory Research Institute (LRRI), and the University of New Mexico (UNM). Our expertise in microfluidics, tissue engineering, nanomaterials, immunology, and toxicology uniquely positions us to develop and apply this highly innovative platform.

Summary of Accomplishments:
We successfully advanced technology for creating thin (1 micron) nanofiber membranes that are created from biological material (peptide charged peptides) and can easily be suspended in microfluidic devices. Such an interface is a key need in tissue engineering and also distinguishes our alveolar/capillary two-compartment in vitro model.

Different tissue layers (endothelial and epithelial) have been successfully cultured on conventional membranes as well as our advanced nanofiber membrane. Not only were transformed cell lines successfully cultured, but also primary cells that are more difficult to work with but yield a more accurate in vitro model. Developing the methods to grow a mimic from primary cells distinguishes our model from other efforts in this area.

Microfluidic architectures have been designed for establishing the two-compartment tissue model. Key challenges that have been met include a platform that provides easy access to both tissue layers of the suspended membrane. Simple-to-operate yet well-controlled microenvironment with options to introduce nanoparticle challenges, perfuse media, sample media, and image tissue layers are all key elements of the platform that poise the platform for a variety of applications. The platform design also accommodates integration with our advanced molecular diagnostic platforms. This will enable rapid, sensitive, integrated detection of important tissue response markers important in determining toxic responses.

Significance:

The proposed research aligns with the nanotechnology safety and characterization goals of the National Nanotechnology Initiative, the National Research Council, and DOE. The proposed research will support the national security mission relating to undesired nanoparticle exposure, and significantly enhance nanomaterial toxicity screening and testing capabilities. This project will also facilitate nanotoxicology assessment and screening of novel nanomaterials developed at the DOE-funded Center of Integrated Nanotechnology in New Mexico. The developed technologies are well aligned with recent Defense Threat Reduction Agency (DTRA) and Defense Advanced Research Projects Agency (DARPA) calls. Our technology developments are complementary to efforts at Los Alamos National Laboratory (LANL) and LRRI, and this work may become an important part of multidisciplinary research efforts in areas of therapeutic screening, nanotoxicology, and infectious disease research.

Luminescent Lanthanide Reporters for High-Sensitivity Novel Bioassays
157690

Year 1 of 3
Principal Investigator: M. Anstey

Project Purpose:
Biological imaging and assay technologies rely on fluorescent organic dyes as reporters for a number of interesting targets and processes. However, limitations of organic dyes such as small Stokes shifts, spectral overlap of emission signals with native biological fluorescence background, and photobleaching have all inhibited the development of highly sensitive assays. The polymerase chain reaction (PCR) is a current work-around for increasing sensitivity, but PCR can introduce bias into the sample and complicate data interpretation. In addition, a need is arising for identifying multiple targets for biomarker discovery or pathogen detection from a bioterrorist attack. These multiplex assays are currently expensive and complex, utilizing microarray plates or multiwavelength excitation/emission detection systems, which limit their application. What is needed is a new type of fluorescent moiety that offers improved properties over organic dyes, enables cost-effective multiplexed analysis, and provides opportunities for new and novel high-sensitivity bioassays.

To overcome the limitations of organic dyes for bioassays, we propose to develop lanthanide-based luminescent dyes and demonstrate them for molecular reporting applications. This relatively new family of dyes was selected for their attractive spectral and chemical properties. Luminescence is imparted by the lanthanide atom and allows for relatively simple chemical structures that can be tailored to the application. The photophysical properties offer unique features such as narrow and non-overlapping emission bands, long luminescent lifetimes, and long wavelength emission, which enable significant sensitivity improvements over organic dyes through spectral and temporal gating of the luminescent signal.

Growth in this field has been hindered due to the absence of the necessary advanced synthetic chemistry techniques and required access to experts in biological assay development. At Sandia, a multidisciplinary partnership between chemistry, biology, and engineering will allow this project to advance the state of the art.

Summary of Accomplishments:
The first course of action on this project was to construct the organic architectures that would simultaneously encapsulate and electronically excite the lanthanide atom in question. Because our synthetic methodology is based around the “Click” reaction developed by Prof. Barry K. Sharpless, several azide and alkyne substrates were made. Some examples include 2-ethynylphenol, methyl 2-ethynylbenzoate, methyl 6-ethynylpicolinate, methyl 6-azidopicolinate, tris(2-azidoethyl)ammonium chloride, methyl 2-azidobenzoate, methyl 3-azidobenzoate, and 1-azido-2-methoxybenzene. Along with the synthesis of these molecular building blocks, a proof of concept experiment was performed to verify that the “Click” chemistry would work in this application. A full ligand, 3,3',3''-(4,4',4''-(nitrilotris(methylene))tris(1H-1,2,3-triazole-4,1-diyl))tribenzoic acid, was made. Two lanthanides, Europium and Terbium, were encapsulated by the ligand and fluorescence studies will begin in the coming weeks. Two other ligands were recently synthesized on a test scale. They are based on picolinate and phenolate molecules, and scale up of the syntheses has begun.

During this time, a computational collaborator at Sandia California was identified and investigations into the excited state electronics of these complexes are under way. The program, GaussView 5.0, is being used as a molecular modeling aid, and the eventual computational work will be performed on Sandia's supercomputer Red Sky using a proprietary molecular orbital energy minimization algorithm. Three additional synthetic chemistry collaborators have been identified who are interested in aspects of lanthanide luminescence (inorganic extended solids, hybrid gold-lanthanide materials, and organic chromophore architectures). Project development discussions are under way and in one case, the ligand 3,3',3''-(4,4',4''-(nitrilotris(methylene))tris(1H-1,2,3-triazole-4,1-diyl))tribenzoic acid is being shared to investigate its radiation-induced scintillation properties.

Significance:

A robust, cost-effective, and multiplexed fluorescent reporter system would be an invaluable tool for the detection of biological molecules in clinical and environmental samples. If successful, this project will provide the DHS, DoD, and DOE with an alternative to current organic dyes in assays specifically geared towards bioterrorism. The Center for Disease Control also demands similar advances in diagnostic medicine, and a successful lanthanide reporter system can provide that advancement in the form of improved fluorescence imaging, magnetic resonance imaging (MRI), and bioagent detection.

Pathogenicity Island Mobility and Gene Content
158185

Year 1 of 3
Principal Investigator: K. P. Williams

Project Purpose:
Key goals towards national biosecurity include improved methods for diagnosing pathogens (natural or engineered), predicting their emergence, and developing vaccines and therapeutics. These goals could be achieved, in part, through a comprehensive analysis of bacterial genes that promote pathogenicity and the mobile DNA elements (pathogenicity islands) where such genes typically reside. Our current knowledge of bacterial pathogenicity genes is extremely limited, and typically based on painstaking laboratory study. This project will develop an automated system to identify islands as soon as genomes are posted at GenBank, and to analyze island gene content and mobility. The resulting island database will address a cyberinfrastructure need, and moreover, provide a short list of potential pathogenicity genes in a new pathogen, enabling deeper bioinformatic island analysis that may allow positive identification of novel pathogenicity genes.

Multiple islands can accrue throughout a genome to combinatorially enhance or modulate pathogenicity. Diverse islands can even appear in tandem arrays at genomic integration hotspots, a configuration promoting inter-island recombination events that may produce new islands with novel gene combinations. The proposed database will enable an in-depth analysis of island genomic sites and arrangements, as well as their phylogenetic distributions, to shed light on how island mobility, evolution, and functional cooperation promote pathogenicity.

Pathogenicity islands are poorly understood and present unique challenges for study, but meeting these challenges to better understand island nature, especially learning how to identify the cryptic pathogenicity genes they may carry, can offer tremendous payoffs for human health, microbial ecology, and biosecurity.

Summary of Accomplishments:
1. The pan-genome alignment program has been reactivated and applied to the 16 available Rickettsia genomes. Results were poor relative to previous results for *Brucella*, ascribed to more repetition and genomic rearrangement. An attempt at mitigation has been started, identifying all landmark genes common to all fully sequenced genomes, removing the 5% of these that cause the most chromosomal breaks when present, aligning these genes relative to the genome that causes the fewest chromosomal breaks after normalizing for phylogenetic distances, and then inserting and aligning remaining genes in the spaces between the landmark genes.

2. While identifying transfer RNA (tRNA) genes as potential genomic-island insertion sites, a large number of a different type of mobile DNA, the self-splicing group I intron, was discovered. Group I introns were previously known from 4 different settings within tRNA genes. This discovery brings this number to 12.

Significance:
A major national security goal shared by DOE and DHS is to enhance the detection of weapons of mass destruction, including biological systems. Focusing on the detection of the genes most responsible for disease, and their genomic neighborhoods, refines biothreat risk assessment and facilitates the detection of novel (possibly engineered) settings for such genes. Since genomic islands control not only

pathogenicity, but also pathways of environmental response, symbiosis, and unusual catabolism, a genomic island database will improve our understanding of microbial ecology.

Production of Extremophilic Bacterial Cellulase Enzymes in *Aspergillus niger*
158186

Year 1 of 3
Principal Investigator: J. M. Gladden

Project Purpose:
Lignocellulosic biofuels hold great promise for dramatically reducing the US dependence on foreign oil. These technologies aim to convert sugars derived from plant biomass feedstocks into biofuels. Current biofuel processing configurations operate under mesophilic conditions, but there is a push toward thermophilic conditions for a variety of reasons, including reduced contamination, more efficient fuel recovery, better enzyme kinetics, and higher metabolic rates, all of which would significantly reduce costs for biofuel production.

A few companies have already begun developing thermophilic biofuel production hosts, but have yet to complete the thermophilic bioprocessing configuration by developing a cellulase cocktail. The thermophilic biofuel system offers several advantages over current mesophilic approaches, most importantly, the significant reduction of opportunistic microbial infection. Commercial cellulase cocktails are derived from filamentous fungi that produce very high enzyme titers, essential for commercialization. Unfortunately, these enzymes are inactive at high temperatures. Thermophilic bacteria produce highly stable thermophilic cellulases and are an excellent alternative. However, bacteria generally produce low titers of these enzymes, an order of magnitude too low. To overcome this barrier, we propose to develop a high-titer thermophilic bacterial cellulase cocktail by expressing these bacterial enzymes in a commercial filamentous fungal host — *Aspergillus niger (A. niger)*.

Our proposed approach would represent the first time an entire bacterial pathway was reassembled in filamentous fungi. We aim to produce the first high-titer thermophilic cellulase cocktail with the potential for significantly reducing the costs of commercial cellulosic biofuels. Expression of bacterial enzymes in filamentous fungi has historically proven difficult because these enzymes are quite foreign to fungi, which leads to poor expression and inhibitory modifications. We will devise a multipronged approach to overcome these barriers, including fusion to fungal enzymes and extensive engineering of the bacterial genes to make them more compatible with fungi.

Summary of Accomplishments:
The goal of this project is to express thermophilic bacterial cellulases in the filamentous fungus, *Aspergillus niger*. To that end, we have selected approximately twenty thermophilic bacterial cellulase genes that have at least some initial activity measurements associated with them through work done at the Joint BioEnergy Institute (JBEI). We have also selected several control genes to validate the expression system we have designed. These control genes include green fluorescent protein (GFP) and several thermophilic fungal cellulases. To date, we have codon-optimized all these genes for *A. niger* and have synthesized all the control genes and four of the bacterial cellulases.

We have also designed an *A. niger* expression vector, called pCB1004-glaA. This vector is based on the glucoamylase promoter from *A. nidulans*, which was chosen since it has been successfully used to express heterologous genes over the last two decades. The vector was designed to add protein tags to the thermophilic bacterial cellulases to facilitate detection of their expression and subsequent characterization. The vector also includes genes that will enable rapid transformation and integration into the *A. niger* genome. To date, the vector has been designed and constructed, and several of the aforementioned control genes and four of the thermophilic bacterial cellulases have been cloned into it.

Significance:

The US Renewable Fuel Standard 2 (RFS2) legislatively mandates 16 billion gallons of non-corn-derived biofuels by 2022 as one step toward reducing our dependence on foreign oil. The DOE has the mission to ensure energy security through reliable, clean, and affordable energy. Our project enables the realization of cost-competitive biofuels derived from lignocellulose through the production of industrially relevant, low-cost enzyme cocktails by recombinant fungi.

Intra-Membrane Molecular Interactions of K^+ Channel Proteins: Application to Problems in Biodefense and Bioenergy
158410

Year 1 of 3
Principal Investigator: E. Moczydlowski

Project Purpose:
The goal of this project is to develop new methods to measure and analyze the structural basis of K^+ channel tetramer stability for applications in biodefense and bioenergy. Ion-selective channel proteins are key effectors of electrophysiological processes linked to cell membrane signal transduction, mechanisms relevant to microbial pathogenesis, and bioenergy production. The aqueous pore of most channel proteins is formed at the central interface of identical or homologous subunits of a torus-like complex embedded within a lipid membrane. All known highly K^+-selective channels from viruses to humans share a structurally homologous pore domain that is a complex of four subunits (homo- or hetero-tetramers). Since integrity and stability of such multisubunit protein complexes is required for assembly and function of most channels, molecular mechanisms underlying intra-membrane protein-protein interactions are of fundamental interest.

The scientific problem addressed by this proposal may be described as follows:
- What is the molecular basis of tetramer stability of K^+ channel proteins?
- How does tetramer stability correlate with ion discrimination, binding affinity, and conductance?
- How do channel functions of ion selectivity, open-closed gating dynamics, signaling, and pharmacology depend on inter-subunit interactions?

Despite intensive research on K^+ channels, the relationship between tetramer stability and channel function remains virtually unexplored. It is known that lowering extracellular K^+ results in loss of function of many K^+ channels; however, the molecular basis of this phenomenon is poorly understood. The scientific challenge is to develop new approaches to measure, analyze, and engineer the molecular specificity and energetic basis of intra-membrane subunit-subunit interactions of K^+ channels. This knowledge can be applied to discovery of new classes of small molecules that disrupt channel function for treatment of human diseases and suppression of pathogenic microbes. It can also be used to design highly stable K^+ channels for engineering of hybrid material nanodevices in the emerging field of bionanoelectronics.

Summary of Accomplishments:
We have begun to analyze residue side chains that contribute to stability of the KcsA channel tetramer. A software analysis tool call PISA (Protein Interfaces, Surfaces and Assemblies) accessed from the European Bioinformatics Institute web site was used to identify molecular contacts at the monomer-monomer subunit interface of the crystal structure of the KcsA tetramer (protein database [PDB] ID: 1K4C). This analysis identified a subunit interface consisting of 37 and 31 residues on adjoining faces of two adjacent monomers. The surface area of the monomer-monomer interface is approximately 1250 $Å^2$. The monomer-monomer subunit interface is stabilized by seven inter-subunit hydrogen bonds and 2 salt bridges. The inter-subunit interface of the KcsA tetramer is formed by contacts between the outer M1 Helix and neighboring M2 Helix, the Pore Helix and M2, the Filter and Pore Helix, the External Loop and Pore Helix, and adjacent inner M2 helices. We have identified the following 40 non-Gly residues at the KcsA tetramer contact interface using PISA as listed according to monomer location: M1 Helix (A28, L41, S44, Y45), Pore Helix (Y62, P63, R64, L66, W67, W68, V70, E71, T72), Filter (T74, T75, V76, Y78, D80), External Loop (L81, Y82, P83), and M2 Helix (R89, A92,

V93, M96, V97, I100, T101, F103, L105, V106, T107, A108, A109, L110, A111, T112, W113, F114, V115). These particular residues are appropriate candidates for alanine-scanning mutagenesis. By measuring the thermal stability of the tetramer formed by each alanine point mutant of these residues, we will be able to assess the free energy contribution of each residue to tetramer stability.

Significance:

This project involves basic research relevant to national security missions of DOE in biodefense and bioenergy. K^+ channels are a frontier area of research in immunology, infectious disease (National Institute of Health [NIH], Defense Threat Reduction Agency [DTRA]), and a recognized drug target for treatment of septic shock in humans. Fundamental knowledge of membrane biology, channels, and transporters is relevant to algae-based biofuel production and other areas of synthetic bioenergy production. Assay methodology and mechanistic knowledge of tetramer stability of K^+ channel proteins may have diverse applications ranging from drug discovery, bioenergy technology, to design of hybrid bionanomaterials with novel electrical properties.

Functional and Robust Asymmetric Polymer Vesicles
158478

Year 1 of 3
Principal Investigator: W. F. Paxton

Project Purpose:
In a living cell, the directional exchange of matter, energy, and information across the membrane is facilitated primarily by transmembrane proteins (TMPs) that are asymmetrically distributed and oriented. Mimicking this asymmetry and function in synthetic hybrid systems is a long-standing challenge in biomolecular and materials science. We seek to understand the principles that govern the reconstitution of TMPs into robust matrices in order to create vesicles that are both radially and axially asymmetric. We intend to 1) explore, systematically, the parameters that govern vectorial insertion of TMPs in robust biomimetic environments and 2) use what we learn to create radially and axially asymmetric hybrid constructs that could be used to regulate the transport of charge in energy production and storage systems and understand signal transduction at immunological synapses between cells and model biomimetic membranes.

Many reports demonstrate that TMPs can be reconstituted into synthetic vesicles and that they retain their activity after reconstitution, yet none have provided a general strategy for controlling the orientation of protein insertion. Furthermore, lipid-based vesicles (liposomes) typically used in reconstitution experiments lack the chemical and mechanical stability required for materials science applications. Polymer-based vesicles (polymersomes) developed over the past decade possess many of the desirable properties of liposomes, while at the same time exhibit remarkable stability relative to their lipid-based counterparts. Our approach to integrating TMPs in biomimetic environments capitalizes on recent developments in: 1) preparing polymersomes, 2) reconstituting TMPs in vesicle assemblies, and 3) synthetic vesicle fusion to prepare robust hybrid structures that are both radially and axially asymmetric. The successful execution of the proposed work will bring new fundamental understanding to the role intermolecular interactions play in protein insertion mechanisms. We anticipate that our approach will afford a versatile platform for integrating TMPs into robust scaffolds that will allow the rational design of an entirely new class of asymmetric biomimetic materials.

Summary of Accomplishments:
We have accomplished the following over the first three months of this project:

- Prepared a preparative scale gel-permeation chromatography system required for the analysis of synthetic polymers involved in this project.
- Characterized commercially available starting materials (amphiphilic block copolymers and functionalized fluorescent dyes) by proton nuclear magnetic resonance (^{1}HNMR) and gel permeation chromatography.
- Prepared fluorescently labeled amphiphilic block copolymers from one of the commercially available polymers. These tagged polymers were purified using a combination of dialysis and size-exclusion chromatography, and then characterized by gel permeation chromatography (GPC).
- Prepared vesicles from these fluorescently labeled polymers using a gentle rehydration strategy and characterized these vesicles via epifluorescence microscopy.
- Prepared azide-terminated silicon wafer surface and used microcontact printing of alkyne inks in the presence of copper to prepare patterned surfaces required for preparing giant unilamelar vesicles via templation.

Significance:
The proposed work is highly relevant to the DOE's efforts to develop biomolecular materials and strategies to self-assemble complex hierarchical structures. Success would represent an important achievement in the design and creation of bioinspired materials that constitute functional systems with emergent synergistic properties. The underlying basic science questions explored will support Sandia's research foundations in Science, Technology and Engineering national security mission, and would contribute to the bioscience and materials science research foundations, with potential practical applications in robust biosensor design and materials capable of transducing and storing energy in the form of ion gradients across synthetic membranes.

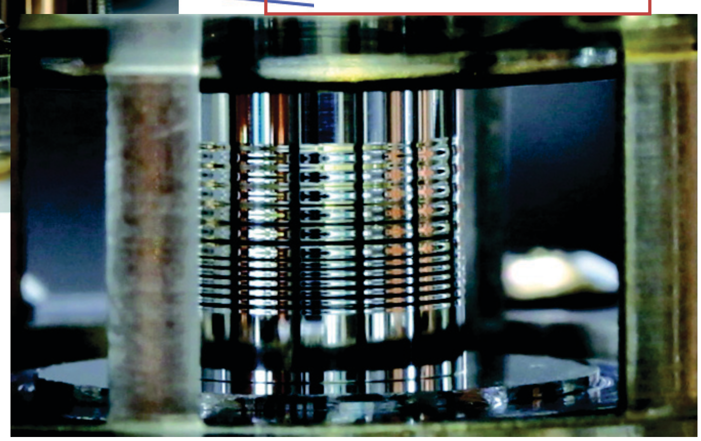
SCIENCE OF EXTREME ENVIRONMENTS INVESTMENT AREA

The Science of Extreme Environments (SEE) investment area seeks to create new knowledge that enables revolutionary advances in the areas of high energy density physics, radiation sciences, pulsed power, and fusion energy for national security needs. A synergistic combination of experiments and theory provides insights into the nature of electronics under exposure to x-rays, gamma rays, neutrons, and other charged particles, and enables the production of high power density x-rays from impressive pulsed power systems. Theoretical computational studies reveal the nature of the complex plasmas formed, and aid in such pursuits as the production of high power microwaves for missile defense. This investment area clarifies scientific understanding about environmental conditions rarely encountered in everyday experience (except, for example, rare situations such as lightning), but which are nevertheless commonplace in several Sandia national security mission areas.

Stability of Fusion Target Concepts on Z
Project 141537

This project, recipient of an FY 2011 Defense Programs Award of Excellence, is studying the application of pulsed power from Sandia's Z machine to generate the compression and heating of matter—particularly deuterium fuel—inside magnetized liners of various materials. While the studies are of importance to the nuclear weapons program, they may also offer a route to inertial confinement fusion ignition of deuterium in beryllium liners that could at least reach break-even energetics, that is, the energy required to achieve ignition of the fuel would be at least equaled by the energy liberated through nuclear fusion (of deuterium nuclei to produce helium plus liberated energy). While this would normally require matter to be compressed and heated to pressures in the range of 100 to 1000 Gigabars, such Magnetized Liner Inertial Fusion (MagLIF), reduces the required pressure to about 10 Gigabars.

Left: Experimental setup on Z; below: closeup of cylindrical liner in which the fuel is contained

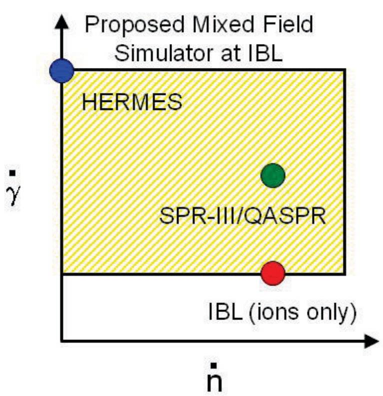


The key scientific issue for the MagLIF concept is the stability of the annular cylindrical liner used to compress the fuel. The outer surface of the liner is susceptible to the Magneto-Rayleigh Taylor (MRT) instability, and this project has studied and modeled this phenomenon, at first using aluminum liners, and subsequently fabricating and studying beryllium liners—the recent development of 6 keV backlighting enabling the simultaneous study of the inner and outer surfaces of the imploding liner. This project will advance understanding of fusion plasmas, the stability of z-pinches, and may ultimately be useful for fusion-fission hybrid concepts. During FY 2010-11, the experimental team pursued controlled studies of the stability of liner implosions and the key physics of the overall MagLIF concept and documented this work in a publication. The MagLIF concept was refined using simulations validated by experimental data and a new high-gain fusion target was designed that will increase the utility of this concept, potentially enabling a future fusion power facility.

Mixed Hostile-Relevant Radiation Capability for Assessing Semiconductor Device Performance

Project 141535

In order to improve validation of semiconductor device performance in hostile environments—an issue relevant to the nuclear weapons, space, and other programs—this project is devising a means to experimentally introduce chips to the combined effects of high-dose-rate ionizing radiation and displacement damage. Existing radiation test facilities cannot probe the combined effects without extraneous background radiation. Ionizing irradiation will be produced by pulsed electron and laser beams, with displacement damage introduced by pulsed high-energy Silicon ions, in order to create a high-fidelity simulator of the threat environment.



Plot of the gamma and neutron flux phase space available using the mixed hostile-relevant radiation capability.

The ability to independently control both the magnitude and timing of ionization and displacement damage will permit simulation of unique neutron-gamma radiation exposures, exploration of synergistic effects, and confirmation of device physics models in previously inaccessible regimes. This project will incorporate results from the Qualification Alternatives to SPR (QASPR) program that demonstrated the ability of high-energy ion exposures to simulate the effects of high flux fast neutron (SPR-III) environments using a range of energy/ion combinations depending on the device geometry and desired damage profile.

Science of Extreme Environments Investment Area

Advanced Tactical HPM System via NLTL and LWA
130802

Year 3 of 3
Principal Investigator: J. J. Borchardt

Project Purpose:
DoD requires tactical high-power microwave (HPM) systems that disrupt or damage electronics in operational environments. Current HPM systems suffer from bulk and weight of radio-frequency (RF) source ancillary systems. The purpose of the project is to develop the nonlinear transmission line (NLTL), a novel HPM RF source component. The NLTL potentially offers transformative capabilities for tactical HPM systems via frequency tune and high repetition rates — without water, vacuum, cathodes, or undesired x-ray generation typical of traditional, relativistic electron beam HPM source technologies. The primary S&T objectives are understanding, modeling, and controlling nonlinear RF generation and scaling NLTL devices and materials to very high powers. This project may ultimately provide DoD with alternatives to traditional HPM technologies that significantly increase tactical utility of HPM systems.

NLTL research includes modeling of the nonlinear dynamics of NLTL, creation of a low-power NLTL for rapid experimental iteration assessment/development of nonlinear electromagnetic materials for high-power scaling; and design, construction, and demonstration of a prototype high-power NLTL. The anticipated benefit of this research is increased tactical utility of future HPM weapons systems through significant increase in power on target per unit system size/weight, as well as significant reduction in HPM system platform integration constraints. The elevated risk in this project derives from the fact that significant basic research on scaling NLTL powers to the gigawatt regime remains undone (e.g., modeling and materials research). While the potential rewards of this research are great, the technological barriers are commensurate.

Summary of Accomplishments:
Over its lifetime, this project has achieved its original development goals. Beginning in FY 2009, we developed a series of low-power magnetic NLTL prototypes using printed circuit board construction. We achieved reasonable agreement between experiment and a simple NLTL nonlinear circuit model and demonstrated several interesting operational regimes, including the "backward wave" regime. Another demonstrated operating regime is a novel result of this project. Both regimes are very important from an HPM system perspective; for example, backward wave operation leads to significantly longer RF pulse output. This potentially increases HPM target effectiveness by delivering more RF energy to the target per pulse. Additionally, we completed an electromagnetic design of a prototype high-power magnetic NLTL during FY 2010. We used a commercial finite element solver to predict and refine the RF performance of the design geometry. This data was compared with a solution of the equivalent circuit that incorporated measured parameters of candidate nonlinear magnetic materials. Parts were fabricated during FY 2010 and in early FY 2011 these parts were assembled. The NLTL was tested and its experimental performance was compared against that predicted by the nonlinear circuit model developed in FY 2009. Some discrepancies were noted, and we attempted to resolve this issue by building and testing a simple nonlinear device, the magnetic shock line, in a similar regime as that in which the high power NLTL was operating. Despite the discrepancies, all the major features explored in the FY 2010

low power, printed circuit board NLTL were demonstrated at high-power/high-voltage in FY 2011. The experimental effort culminated with a demonstration of the unique capabilities of NLTL.

Significance:

The core R&D accomplishments of this project are significant to the general S&T community as well as relevant to Sandia's national security mission areas. With respect to the latter, the need for nonlethal, counter-materiel weapons to enhance US capability in conventional and irregular warfare is well established. For example, the Department of Defense 2006 *Quadrennial Defense Review* identifies nonlethal technologies as a needed capability to combat both terrorism and weapons of mass destruction threats. HPM technology is identified as a key capability in the Major Combat Operations Joint Operating Concept document and other DoD planning documents. As such, novel HPM source technology development that enables fundamental new capabilities (such as frequency tuning and high repetition rates) while reducing size, weight, power, and ancillary system requirements in fielded, tactical systems directly supports DoD technology strategy. Thus, this project falls well within Sandia's national security mission space.

Several other important potential applications for the research undertaken in this project are of interest to the general S&T community. Nonlinear dielectric, nonlinear magnetic, and electromagnetic shock wave phenomena are of general interest to many science and engineering disciplines. For example, nonlinear pulse sharpening devices can provide unique capabilities in pulsed power research systems, as demonstrated in the Sandia repetitive high-energy pulsed power system. Reduced pulse rise times and refined pulse shaping capabilities in high-energy-density physics and inertial confinement fusion facilities such as the Z Machine are also possible with the use of nonlinear and electromagnetic shock phenomena. In addition, NLTL technologies developed within this project in particular could potentially serve as compact, high-power RF sources in some radar applications (e.g., air traffic control) and charged particle accelerator applications (e.g., linear accelerators). In particular, compact, high-reliability, and low-cost particle accelerators are desired for medical radiation therapy facilities.

Confinement of High-Temperature Laser-Produced Deuterium Plasmas Using Pulsed Magnetic Fields
130804

Year 3 of 3
Principal Investigator: K. W. Struve

Project Purpose:
Experiments have shown that intense ultrafast lasers can ionize small frozen-gas clusters with hundreds to thousands of atoms to produce high ion-temperature plasmas. These clusters are produced in vacuum with expanding jets of cooled gases. This phenomenon has been exploited to produce fusion neutrons from deuterium clusters. Because ion temperatures exceeding 10 keV are achievable, it is possible to produce fusion yields with laser pulses of a few joules to a few hundred joules. The neutron yield in these experiments is limited by the fast disassembly time (< 100 ps) of the deuterium plasma. Yield might be increased if plasma expansion could be slowed with an external magnetic field. At the densities of these plasmas ($\sim 10^{19}$ /cm^3), a magnetic field approaching 100-200-T is needed. This work is a collaboration between Sandia and the University of Texas, and is aimed at placing a magnetic field around a deuterium cluster plasma heated by the Sandia Z-Petawatt or the Texas-Petawatt lasers. It involves building a portable 2 MA pulsed power supply to drive a 2 MG coil in a vacuum chamber at the focus of a petawatt laser, to solve potential issues of coil breakdown, and use this field to explore neutron yield enhancement. Challenges for this work are that of producing a portable (or transportable) 2-MA pulsed current source, delivering this current to vacuum, and producing these intense magnetic fields in the presence of gas clusters and uncondensed gas without shorting of the coil, which at these currents and fields is destroyed with each shot.

Summary of Accomplishments:
The goal of this project has been to conduct cluster fusion experiments with 200-T magnetic fields on the Texas Petawatt laser at the University of Texas, to determine if magnetic fields can increase neutron output from such plasmas. These experiments have not yet been done, but all the tools needed for these experiments are now available to the university, with experiments planned for spring of 2012. With this project, we have designed and built a device that can be moved to a large laser facility that delivers current to a magnetic field coil in a vacuum chamber. The initial design was a 50-T, 500-kA prototype that was designed to test both the pulsed-power concept and a unique technique to get power into the vacuum with very little inductance penalty. With this device, we were able to test single-turn coils at the 50-T level, determine vacuum requirements to avoid electrical breakdown in the vacuum insulator and vacuum transmission lines, and inject deuterium and surrogate clusters into the coil region without shorting the coil feed. This was done by insulating the inner surface of the coil, but also by providing access to inject clusters perpendicular to the axis of the coil since laser access is required along the coil axis. Based on the experience with the 50-T system we designed and built a 2-MA, 200-T system that is now being fielded at the university. With this system, we have been able to achieve 1-MA, 100-T operation in air at half charge voltage. Related work is proceeding under the aegis of a separate collaboration to extend to vacuum operation with cluster injection at the 2-MA level. Yet to be addressed are issues related to controlling debris and protecting equipment from the exploding coil, and measurement of the magnetic field, prior to cluster fusion experiments with the laser.

Significance:
Sandia has unique state-of-the-art pulsed power and laser facilities to support stockpile stewardship. The strategic goals of this initiative are to help maintain US leadership in the physical sciences, encourage collaborations between university researchers and national laboratory scientists, and improve the quality of science within the weapons mission. This project is well aligned with Sandia's mission

responsibilities for operating and stewardship of our large high energy density (HED) facilities. This project involves collaboration with scientists from the University of Texas at Austin and strengthens an ongoing strategic partnership between Sandia and the University of Texas System.

Modeling Ramp Compression Experiments Using Large-Scale Molecular Dynamics Simulation
130807

Year 3 of 3
Principal Investigator: A. P. Thompson

Project Purpose:
Sandia is among the world leaders in characterizing materials in off-Hugoniot regions of phase space using experimental ramp-wave loading. However, leadership in dynamic material response also requires state-of-the-art theory and modeling. Molecular dynamics simulation (MD) is an invaluable tool for studying problems sensitive to atom-scale physics such as structural transitions, non-equilibrium dynamics, and elastic-plastic deformation. There are, however, significant difficulties in utilizing MD for extreme environments. First, current atomic potentials are based on ambient material properties and are inadequate for multi-megabar and high-temperature regimes. Second, ramp loading on Z, shock-induced transitions, and melting occur over timescales too long to be simulated with today's methods, which are systematically limited to timescales of 0.1–1 nanoseconds.

By generalizing recent innovative methods developed for shock loading, we propose to extend MD timescales by 3 orders of magnitude, enabling us to model ramp compression and other longer-timescale phenomena. We will develop new interatomic potentials specifically for extreme environments. We will develop and implement expressions for calculating plastic strain and dissipative work. Our primary application will be to recent flyer-plate experiments on Z that have shown a gradual drop in wave speed near melt in beryllium. This response is not captured by continuum models.

Summary of Accomplishments:
The goal of this project was to develop molecular dynamics capabilities enabling computational simulation of material response under ramp-loading conditions. The techniques we have developed fall into three categories: 1) molecular dynamics methods, 2) interatomic potentials, and 3) calculation of continuum variables. Highlights include the development of an accurate interatomic potential describing shock-melting of beryllium, a scaling technique for modeling slow ramp compression experiments using fast ramp MD simulations, and a technique for extracting plastic strain from MD simulations. All of these methods have been implemented in Sandia's Large-Scale Atomic/Molecular Dynamics Simulator (LAMMPS) MD code, ensuring their widespread availability to dynamic materials research at Sandia and elsewhere. This work also produced advances in our understanding of dynamic response of several materials, including beryllium, aluminum, polymer, polymer foams, germanium and silicon.

Significance:
The techniques developed in this project will contribute to the understanding of shock and quasi-isentropic physics relevant to NNSA interest in the dynamic materials response of beryllium and other materials, and to DOE inertial confinement fusion (ICF) applications, as well as expanding understanding of several other important areas of material behavior.

Refereed Communications:
R.E. Jones, J.A. Zimmerman, J. Oswald, and T. Belytschko, "An Atomistic J-Integral at Finite Temperature Based on Hardy Estimates of Continuum Fields," *Journal of Physics: Condensed Matter*, vol. 23, p. 015002, January 2011.

J.A. Zimmerman, J.M. Winey, and Y.M. Gupta, "Elastic Anisotropy of Shocked Aluminum Single Crystals: Use of Molecular Dynamics Simulations," *Physical Review B*, vol. 83, p. 184113, May 2011.

New Density Functional Theory Approaches for Enabling Prediction of Chemical and Physical Properties of Heavy Elements
130808

Year 3 of 3
Principal Investigator: A. E. Mattsson

Project Purpose:
Density functional theory (DFT) is the preferred computational method for exploring materials properties, and Sandia scientists are at the forefront of DFT-based equation of state (EOS) construction, where information from both experiments and computational investigations are used. However, present DFT techniques are not adequate for f-electron materials, hampering our ability to computationally investigate many materials of high interest to DOE/NNSA, such as plutonium (Pu), under conditions where experiments are hard and/or very expensive to perform. We propose to remedy the two major deficiencies preventing DFT calculations from providing accurate properties also for actinides and lanthanides: inaccurate exchange-correlation functionals, and inappropriate spin and relativistic treatment.

Sandia has a unique opportunity to develop differentiating computational tools for f-electron materials. The Relavistic Spin Polarised (test) (RSPt) code from Los Alamos National Laboratory (LANL), already used at Sandia, is specifically designed to handle f-electron materials. However, relativistic effects need to be taken into account non-perturbatively in those systems. We are exploring this important physics and implementing it into a branch of the RSPt code. Available DFT functionals are not accurate enough to capture the complex interactions in f-electron systems. We are developing a new functional appropriate for f-electron systems using the promising subsystem functional scheme, recently created by Nobel Laureate W. Kohn, A.E. Mattsson, and R. Armiento.

Solving those challenging fundamental problems will enable quantitative prediction of the behavior of heavy element materials under normal and extreme conditions, for the benefit of the entire Nuclear Weapons (NW) complex.

Summary of Accomplishments:
This first implementation of Dirac Density Functional Theory is providing immediate insight into the role of relativity in lanthanide and actinide materials. Compared to calculations previously considered state of the art, the Dirac treatment gives a substantial change in equilibrium volume predictions for materials with large spin-orbit coupling. With the new diracRSPt code, we have shown that full relativistic treatment is indeed necessary for treating actinides. The treatment considered state of the art up until now, a variational inclusion of spin-orbit coupling, is not adequate, not even as a reasonable starting point. For a full capability, a DFT functional capable of describing strongly correlated systems needs to be developed. A not-as-yet tested functional has been developed and insights gained. Dirac Density Functional Theory is now a permanent part of the RSPt code, and together with the new understanding of functional issues, it will permit us to gain more fundamental understanding, both quantitatively and qualitatively, of materials of importance for Sandia and the rest of the Nuclear Weapons complex.

Significance:
Developing improved models of plutonium EOS and strength through focused tri-lab projects such as the Dynamic Plutonium Experiments and the National Boost Initiative is one of the highest DOE/NNSA priorities. Generating high quality EOS and strength data, primarily through the design and execution of Z experiments, is a key aspect of Sandia's dynamic materials mission. Improving DFT's ability to

theoretically predict plutonium properties will broaden the scope of Sandia's contributions. Improved ability to computationally investigate chemical and physical properties of heavy elements will also provide an enhanced science base for technologies needed for, for example, nuclear fuels/waste forms, and fusion reactors.

Refereed Communications:

M.T. Lusk and A.E. Mattsson, "High-Performance Computing for Materials Design to Advance Energy Science," *MRS Bulletin*, vol. 36, pp. 169-177, March 2011.

Study of Radiative Blast Waves Generated on the Z-Beamlet Laser
130809

Year 3 of 3
Principal Investigator: A. Edens

Project Purpose:
We propose to study the physics of astrophysical radiating blast waves by studying radiating blast waves produced using the Z-Beamlet laser system. Our primary objective will be to understand, in greater detail, how blast waves evolve when they have entered a strongly radiative phase, a regime often entered by many supernova remnant blast waves. This project has three primary goals. First, to observe the oscillation of a perturbation on a blast wave surface, given that these oscillations are a key component of several astrophysically relevant instabilities, but have never been observed experimentally. The second objective is to develop a direct measurement of the density and temperature across the shock front to quantitatively compare theoretical predictions to experimental results. This would result in the best-diagnosed set of radiative shocks produced by such an energetic laser system. The final observation is the confirmation of a growing instability (the Vishniac instability) hinted at in previous experiments.

This work is motivated by a desire to probe various hydrodynamic theories and simulations forwarded in the astrophysical literature which predict the growth of instabilities on shock fronts in strongly radiating blast waves, in particular the Vishniac instability. These instabilities are thought to give rise to much of the spectacular structure observed around supernovae remnants. The predictions of the Vishniac instability theory are that its evolution should be determined by two parameters, the wavelength of perturbations and the polytropic index of the gas. By varying these parameters and comparing the observed perturbation evolution to theoretical predictions, we are able to quantitatively test this astrophysical theory with laboratory experiments. Our measurements would result in a new level of quantitative understanding of these astrophysically relevant radiative shocks. These experiments, a collaboration, leverage the unique facility capabilities of Sandia with the spectroscopic measurement and analysis expertise of the University of Texas.

Summary of Accomplishments:
We upgraded the probe laser at the Z-Beamlet facility to fire 4 pulses with 250 ns interval between pulses. This improvement should allow for increased data return for any experiments that utilize probe laser diagnostics and have a compatible characteristic timescale. The time and energy scales involved turned out to be significant challenges, as they lie in a regime between that achievable by physical pulse stacking and those achievable easily with electronic measures. In addition, we designed and procured parts for a spectroscopic diagnostic to be used at the Z-Beamlet facility. This diagnostic can increase the range of capabilities of the facility.

Significance:
Sandia has unique state-of-the-art pulsed power and laser facilities that have historically been used by national laboratory scientists to conduct research supporting stockpile stewardship. The Department of Energy has recently directed NNSA and the national laboratories to open up access of the nation's large high-energy-density science facilities to the broader national research community to answer fundamental questions at the forefront of scientific knowledge. This project is well aligned with Sandia's new mission responsibilities for operating and stewarding our large high energy density (HED) facilities. This project will also further an established strategic partnership between Sandia and the University of Texas System.

Advanced K-Shell X-Ray Sources for Radiation Effects Sciences on Z
141533

Year 2 of 3
Principal Investigator: B. M. Jones

Project Purpose:
The Z machine provides intense 1–10 keV photon energy x-ray environments for radiation effects science (RES) experiments using wire array and gas puff loads. This project seeks to extend the portfolio of x-ray sources available on Z to >10 keV photon energies by exploring a novel load configuration. This project is allowing us to explore the parameter space of these loads and assess their applicability to x-ray generation.

Summary of Accomplishments:
Our initial series of experiments on the Z machine demonstrated K-shell x-ray emission at >10 keV. In September 2011, we executed our second series on Z. We made improvements to our targets from the first series, and also were able to evaluate another novel target design. An excellent data set was collected, and we anticipate that this will help in the physics understanding of these sources. A particular emphasis of this project is to use numerical modeling to design the experiments, and then test the models using measured data. Benchmarking to the initial Z experiments has guided improvements to the models which have provided better consistency in the September 2011 data set.

Significance:
This work is relevant to DOE strategic needs in nuclear weapons stewardship (providing higher photon energy sources and potentially higher yields for RES work on Z), and improves the capacity of existing facilities for more sophisticated scientific research (basic physics of pulsed-power-driven x-ray sources).

High Peak Power / Pulse Energy Laser Sources
141534

Year 2 of 3
Principal Investigator: R. Bambha

Project Purpose:
High-performance lasers can perform key tasks in areas such as high current switching and probing using ultrashort pulses, but suitable lasers have typically been very unwieldy. Compact lasers capable of producing diffraction-limited pulses with energies of 1–10 mJ and subnanosecond duration are desirable but not currently available. Current laser systems, such as mode-locked Ti-sapphire and microchip master oscillator power amplifier (MOPA) architectures employing low gain bulk amplifiers, are inherently large and may require multiple stages of amplification, increasing cost, size, and complexity. We propose to build lasers that can achieve all the desired optical properties simultaneously in a compact size by leveraging recently developed phosphate glass fibers with very high rare-earth (RE) doping concentration. Phosphate glass can accommodate RE doping levels approximately 20 times higher than convention fused silica. This feature enables high gain, single-stage, mJ-level amplifiers with lengths of only a few centimeters, nearly eliminating the nonlinear effects that limit energies in conventional silica fibers. The proposed approach is expected to reduce cost, size, and weight of the system while preserving diffraction-limited beam quality. Furthermore, phosphate glass has a large amplification bandwidth, offering wideband pulse amplification at wavelengths previously unavailable using crystalline hosts.

This project aims to create fiber amplifiers that surpass the performance of previous fused silica fiber amplifiers by using phosphate glass, which has substantially different properties that are not entirely characterized. In order to achieve this end, we will develop new methods for measuring and optimizing this unconventional fiber and adapt our efforts to achieve our programmatic milestones as our knowledge grows. As a result of this project, Sandia is attaining a unique knowledge base for building pulsed phosphate glass fiber amplifiers. Collaboration between the fiber amplifier developers and the developers of pulsed-power and sensor systems will allow amplifiers to be optimized for new applications.

Summary of Accomplishments:
We have made significant progress in pulse energy, thermal management, glass characterization, seed laser development, and amplifier modeling. We have passed the 2 mJ milestone with 2.25 mJ from a 5%-doped Yb:phosphate fiber amplifier with a 49 μm core diameter. The limitation was due to optical damage from temporal spikes in the Q-switched fiber laser we used for seeding experiments. Although the Q-switched fiber laser produces large wavelength-tunable pulses, its high gain leads to picosecond spikes on the 10-ns envelope. We have modified a Yb:YAG micro laser to produce a well-behaved seed to facilitate further amplifier experiments at 1.03 microns. Based on published data for phosphate glass we anticipated the damage threshold to be 25 J/cm^2 (1-ns pulse), facilitating 10-mJ pulses using 100-micron-core fibers. We performed damage threshold measurements on phosphate and silicate glasses using a focused Gaussian beam, and we also measured the damage level for fused silica for comparison. From these measurements we discovered that the damage level for phosphate glass was slightly less than that for fused silica (approximately 20% lower) and approximately 40% higher than silicate glass; also, the measured damage threshold for phosphate glass appears to be higher than the published limits.

We built a compact fixture allowing the phosphate fiber to be cooled directly using water, and this allows short (< 20 cm) fibers to be pumped continuously with at least 20 W. Significant effort was also invested to develop methods for tapering and mode-matching fibers to maintain beam quality.
We have developed a dynamic fiber-amplifier model and a numerical simulator that is temporally, spectrally, and spatially resolved, allowing control of amplifier parameters and seed pulse characteristics. The model compares well with published results and the simulator runs under MatLab using available parallel processing capability. The simulator will assist in optimization of the amplifier.

Significance:
Fiber amplifiers are generally attractive for applications in which good beam quality, high gain, and a compact device are desired, but output energies of fiber amplifiers have been limited by optical damage and spectral distortion to levels below a few hundred microjoules. This project has demonstrated the potential for highly doped fibers to amplify optical pulses into the multi-millijoule range using very short fiber lengths that mitigate spectral distortion and maintain high optical quality. Application areas that would benefit from improved optical transmitters include remote chemical sensing and high-resolution LIDAR (light detection and ranging). National security areas that stand to benefit include intelligence gathering, reconnaissance, and disaster response. Additionally, fiber amplifiers with low nonlinearity could simplify chirped-pulse amplification chains used in ultrashort-pulse fiber laser systems. The spectral properties and beam profiles that are needed to realize important applications are typically difficult to attain using oscillators operating in the millijoule range, but the desired optical properties are often achievable at lower energies using diode or fiber lasers. Fiber amplifiers with low distortion afford the possibility of generating the required spectral properties using low-power lasers and amplification to reach desired power levels.

Well-controlled, millijoule-level optical pulses will potentially allow breakthroughs in sensing. For instance, optical heterodyne detection is a technique that can yield ultrasensitive, shot-noise-limited detection. The use of heterodyne detection with multi-millijoule transmitters, however, has been impeded by a lack of narrowband pulsed lasers. Low-distortion fiber amplifiers could be integral to the outcome of making new heterodyne-detection-based systems practical. Important heterodyne-based sensor applications include remote vibrometry, remote sensing of gaseous chemical species, and high-range-resolution LADAR (laser radar).

Operation at eye-safe wavelengths can be highly advantageous for remote sensing systems. Thulium-doped and holmium-doped fiber amplifiers that will be developed under this project will be well suited for eye-safe systems in the 1.7 to 2.1 micron region. Atmospheric absorption at 2 microns could also be used advantageously for certain high-altitude air-to-air sensors by exploiting the fact that transmissions to and from the ground can be greatly attenuated by atmospheric absorption.

Mixed Hostile-Relevant Radiation Capability for Assessing Semiconductor Device Performance
141535

Year 2 of 3
Principal Investigator: E. S. Bielejec

Project Purpose:
Exploring the combined effects of high dose-rate ionizing radiation and displacement damage is very important to understanding the response of semiconductor devices to hostile radiation environments. Existing radiation test facilities cannot probe the combined effects without extraneous background radiation. To provide a tool for detailed studies of the mechanisms that affect semiconductor device response, we propose combining ionizing irradiation, produced by pulsed electron and laser beams, with displacement damage, introduced by pulsed high-energy silicon ions, to create a high-fidelity simulator of the threat environment. The ability to independently control both the magnitude and timing of ionization and displacement damage will permit: 1) simulation of unique neutron-gamma radiation exposures, 2) exploration of synergistic effects, and 3) confirmation of device physics models in previously inaccessible regimes. Controlled time-dependent ionization will also explore device responses to a range of stockpile-to-target scenarios. By using both electron and laser beam systems to introduce ionization to a device, oxide and bulk Si ionization effects will be independently characterized. A fundamental aspect of this project is research into the unexplored synergistic effects of displacement damage and ionizing radiation. Our goal is to develop a mixed radiation exposure capability that can be used to confirm our understanding of the underlying physics of these unique radiation environments and to evaluate the effects that may arise in new device designs or materials considered for insertion into the stockpile.

The ability to independently control both the magnitude and the timing of high dose-rate ionizing radiation and displacement damage is of interest for both scientific studies exploring synergistic effects and physical simulation of key environments necessary for qualification efforts, and will be a capability unique to Sandia. This project seeks to explore these environments by combining ions for displacement damage and electron and laser beams for ionization.

Summary of Accomplishments:
We have finished integrating the heavy ion, electron and laser systems into a single chamber in the ion beam laboratory, and developed the LabView software necessary to control the combined exposures. The first irradiations combining the pairs of exposures (ion + electron, ion + laser and electron + laser) have all been completed. The main thrust of the work for this fiscal year has been broken down into two areas: 1) continuing to study the enhanced photocurrent annealing that we observed using ion + electron exposures and 2) improving the cross-calibration between the electron and laser ionizing dose rates. In the first area, we have run a series of experiments to explore the dose rate dependence on the enhanced photocurrent annealing using both ion + electron and ion + laser exposures. We observe the following: 1) similar results for both electron and laser exposures with comparable dose rates and 2) that for very short times after the irradiation, the annealing factor greatly increases (indicating more damage with photocurrent) prior to decreasing (indicating less damage or enhanced annealing with photocurrent). These results are preliminary and may be associated with circuit effects, but indicate the importance of understanding and modeling the physical environment. In the second area, we have used the DaVinci technology computer-aided design (TCAD) program to model the photocurrent for both the electron and laser exposures for a simple PIN structure. We find excellent agreement between the model photocurrents and the experimentally measured photocurrents for both electron and laser exposures. This indicates that we have a good cross-calibration between the electron and laser dose rates.

Significance:
The successful completion of this project will improve our basic understanding of the combined ionization and displacement damage environments, and benefit the nuclear weapons complex by providing a means to quantify synergistic radiation effects on electronics in nuclear weapons to the threat environment (considered beyond the scope of the existing Qualification Alternatives to the Sandia Pulsed Reactor [QASPR] program). In addition, the ability to field a programmable, pulsed, gamma-plus-neutron flux simulation tool for simulating the radiation threat environment would be an unprecedented NNSA capability. The improved basic understanding would further Sandia's knowledge of radiation effects and support Sandia's ongoing efforts in radiation hardness assurance testing. This mixed radiation exposure system would provide a simulation fidelity (at the 1 mm^2 scale of device testing) that would exceed that attainable at any other facilities. This capability would greatly benefit future life extension missions and new weapon systems.

Stability of Fusion Target Concepts on Z
141537

Year 2 of 3
Principal Investigator: D. Sinars

Project Purpose:
Achieving inertial confinement fusion ignition in the laboratory requires matter to be compressed and heated to pressures in the range of 100 to 1000 Gigabars. Pulsed power drivers offer efficient, inexpensive ways to heat and compress matter, but it is not yet known if they can reach the tremendous pressures needed for fusion ignition. A new concept, Magnetized Liner Inertial Fusion (MagLIF), reduces the required pressure to about 10 Gigabars by magnetizing and preheating the fusion fuel. Modeling suggests that this concept could lead to scientific breakeven on Z (fusion energy comparable to energy delivered to the fuel).

The key scientific issue for the MagLIF concept is the stability of the annular cylindrical liner used to compress the fuel. In particular, the outer surface of the liner is susceptible to the Magneto-Rayleigh Taylor (MRT) instability, which may be enhanced by an electro-thermal instability. At present, there are no stability studies of liner implosions with drive pressures greatly exceeding the strength of materials, as would be the case for MagLIF. With the recent development of 6 keV backlighting and the ability to fabricate beryllium liners, the Z facility provides a unique venue to simultaneously study the inner and outer surfaces of the imploding liner. This will be important in determining the liner integrity during the implosion. The goal of this project would be to understand the stability of cylindrical implosion systems relevant to the MagLIF concept.

This project will study a new, high-risk fusion concept that will advance our understanding of fusion plasmas, the stability of z-pinches, and which may ultimately be useful for fusion-fission hybrid concepts. The concept is not a high-gain system, which has been the traditional focus of the existing sponsored inertial confinement fusion mission.

Summary of Accomplishments:
We are examining the physics of a new inertial fusion concept known as MagLIF, emphasizing the stability of the liner during the implosion. During FY 2010, we designed experiments for the Sandia Z facility that did controlled studies of the stability of liner implosions. We explored the key physics of the overall MagLIF concept and documented this work in a paper in *Physics of Plasmas*. During FY 2011 we analyzed the results of the initial experiments, which studied a key instability under relevant, well-controlled initial conditions for the first time. This work was shared with the community during FY 2011 in two publications and two invited talks. This data, while collected under conditions relevant to MagLIF, is fundamental to a wide range of magnetically driven experiments and applications, a fact recognized by an FY 2011 Defense Programs Award of Excellence. Follow-on experiments studying instability growth seeded by initial surface roughness in beryllium liners were designed and executed during FY 2010–FY 2011. These data are being analyzed and will be ready for publication during early FY 2012, and were shared as an invited oral presentation. The MagLIF concept was refined during FY 2011 using simulations validated by the experimental data and a new high-gain fusion target was designed. The original target design was low-gain and, while capable of high fusion yields, it would primarily have been useful for stockpile stewardship. The high-gain target design will increase the utility of this concept, potentially enabling a future fusion power facility. This research was reported in an invited oral presentation and was submitted to *Physical Review Letters*.

Significance:
This work is relevant to DOE strategic needs in Nuclear Weapons Stewardship, Energy Security (could decrease the cost of future z-pinch driven inertial fusion energy sources), and improves the capacity of existing facilities for higher-impact research. High-quality science in the area of magnetically driven implosions could lead to additional capabilities for and increase the visibility of Sandia within the high energy density physics community.

Refereed Communications:
D.B. Sinars, et al., "Measurements of Magneto-Rayleigh-Taylor Instability Growth During the Implosion of Initially Solid Al Tubes Driven by the 20-MA, 100-ns Z Facility," *Physical Review Letters*, vol. 105, p. 185001, October 2010.

D.B. Sinars, et al., "Measurements of Magneto-Rayleigh-Taylor Instability Growth During the Implosion of Initially Solid Metal Liners," *Physics of Plasmas*, vol. 18, p. 056301, May 2011.

Ultrashort Pulse Laser-Triggering of Long Gap High-Voltage Switches
141538

Year 2 of 3
Principal Investigator: P. K. Rambo

Project Purpose:
Long-gap, laser-triggered high-voltage discharges have numerous applications from super-radiant laser sources and laser wakefield acceleration to laser-triggered spark gaps used for megavolt switching in pulsed power devices to triggered and guided lightning. The problem facing all such efforts is the ability to create long ionized channels with adjustable plasma density and extended plasma lifetimes in order to improve discharge reliability, reduce temporal jitter, and allow for longer gaps and higher hold-off voltages. To overcome these problems, we propose using subpicosecond laser pulses to examine switching aspects in long-gap high-voltage discharges, with special emphasis on extension of plasma lifetime. Prior application of such ultrashort pulse (USP) lasers (instead of the nanosecond pulses more commonly used in pulsed power switching) in state-of-the-art high-voltage switching has focused on different parts of the problem, demonstrating very low jitters with USP lasers at low voltages or demonstrating high-voltage discharges with USP lasers but with no attention to jitter.

The proposed work innovates upon the current state-of-the-art by joining aspects of various former efforts while directly addressing the key issue of improvements in laser plasma density, length, and lifetime. Such advances occur by considering multiple USP and nanosecond laser pulses for the plasma improvements. To do this, complex ionization and recombination dynamics must be properly understood, requiring a systematic study of relevant gas ionization. Subsequently, we will improve ionization and increase the plasma lifetime via methods like multiple ultrashort pulses and additional long pulse heating beams. With sufficiently spatiotemporally improved plasmas, we can leverage unique expertise in pulsed power, lasers, and complex modeling to maximize long-gap switching by these ultrashort pulses. The novel realization of these improvements will yield switches with higher voltage operating points and lower jitters, features desired in future-generation pulsed power machines.

Summary of Accomplishments:
Efforts to quantify the amount of gas ionization with respect to laser intensity were complicated by the convolution of nonlinear Kerr self-focusing and plasma defocusing, which prevented accurate measurement of laser spot size. Subsequently, we developed a novel approach of using wavefront curvature change to measure nonlinear focal shift. Using two different focal geometries allows us to emphasize either self-focusing or ionization. Using a semi-analytical theory to fit both data sets simultaneously provides the ionization data and the self-focusing data.

A variety of techniques for extending plasma spatial extent and lifetime were explored. Plasma lengths were extended via the concatenation of the ionized channels created by multiple ultrashort pulses. In one case, two simultaneous pulses of different energies were self-focused at different positions so as to create a longer combined plasma channel. In another case, input lens chromatic aberration focused different laser harmonics at different spatial positions, stitching together the resultant plasmas. Effective plasma lifetimes were increased both by re-ionization in a sequence of ultrashort pulses and by heating of an ultrashort pulse plasma by a nanosecond-scale laser pulse.

Modeling efforts have approached the laser-triggered switch from the laser ionization perspective and from the streamer development/switch closure perspective. A laser ionization model has been developed and benchmarked, which accounts for diffraction, multiphoton ionization and associated defocus, cascade ionization, Kerr self-focusing, plasma recombination, and group velocity dispersion. In addition, a fully 3D model has been developed of streamer evolution in sulfur hexafluoride switching gas. To our knowledge, this model is the first of its type including the impact of optical plasma emission from streamer tips upon nearby ionization.

A modest switch design has been developed that is commensurate with laboratory and safety constraints. Surplus switch electrodes were obtained, while other electronic parts have been ordered and are pending arrival.

Significance:
In a general sense, low-jitter, high-voltage switches are used in a variety of areas central to DOE's efforts: Pockels cell drivers for lasers, pulsed power science, accelerators, and explosives triggers. In addition, guided long-gap, laser-triggered, high-voltage discharges have been of historical interest to directed energy advocates in their missions.

Specifically, work performed this year has underscored a variety of previously unexplored modest methods for concatenation of plasma channels. While such techniques may be applied to laser-triggered switches, they also would apply to work on the guiding of microwaves with laser-generated plasma channels.

Additionally, modeling efforts can now simulate, reasonably well, the behavior of laser-triggered switches. This capability allows better failure mode analysis and continuous improvement on existing systems, while giving future switch designs a better chance of success.

Refereed Communications:
D.V. Rose, D.R. Welch, R.E. Clark, C. Thoma, W.R. Zimmerman, N. Bruner, P.K. Rambo, and B.W. Atherton, "Towards a Fully Kinetic 3D Electromagnetic Particle-in-Cell Model of Streamer Formation and Dynamics in High-Pressure Electronegative Gases," *Physics of Plasmas*, vol. 18, p. 093501, September 2011.

X-Ray Thomson Scattering Measurements of Warm Dense Matter
141540

Year 2 of 3
Principal Investigator: J. E. Bailey

Project Purpose:
Warm dense matter exists at the boundary between condensed matter and plasma physics and challenges understanding. It is significant for applications, including z-pinch and inertial fusion laboratory experiments, and in astrophysical objects such as white dwarfs and giant planets. Modern high energy density facilities have made it possible to create warm dense conditions in the laboratory. Generating warm dense conditions is challenging, but thorough understanding also requires accurate detailed diagnostics. This project will advance warm dense matter physics by combining x-ray Thomson scattering, a powerful diagnostic for warm dense matter, with extreme environments created at the Z facility. X-ray Thomson scattering uses an intense laser (in this case Z Beamlet) to produce quasi-monochromatic x-rays that probe matter at high density. Measurements of the spectrally resolved scattered x-rays determine both temperature and density. In this project, we intend to develop a flexible capability suitable for diagnosing either shock- or radiation-heated samples. The capability will be exploited to advance cutting edge physics topics selected from candidates such as warm dense matter equation of state, influence of correlations on atoms in dense matter, and white dwarf envelopes.

X-ray Thomson scattering is complex and it has never been employed on any pulsed power facility. The main challenge arises from the fact that the scattering cross section is tiny: the weak desired scattering spectrum must be observed in an environment that produces copious background x-rays. The risk is mitigated by the previous demonstration of x-ray Thompson scattering at laser facilities and by the pre-eminence of Z for creating shock and radiation heated samples. Indeed, the proposed research is exciting precisely because it combines two extraordinary capabilities for the first time to advance physics of a rich new field. It will help establish Sandia as a leader in the exciting warm dense matter field and it will help maintain Sandia leadership in dynamic materials and radiation science research.

Summary of Accomplishments:
During the previous two years, this project has established the foundation for x-ray scattering measurements at Z. In-house Sandia expertise has been developed in this newly established research topic through group meetings and discussions, off-site and on-site consultations with experts in the field, and by exploiting this new knowledge base to design and plan experiments. The key missing technology element, a spherical crystal spectrometer suitable for use at Z, was designed, fabricated, and tested. Calibration capability for this spectrometer was developed and used to measure the spectral resolution, spatial focusing characteristics, and relative reflectivity of candidate crystals. This capability also enabled the first quantitative statistical characterization of x-ray image plate detectors. Experiments were conducted at the Z Beamlet calibration facility to verify that the spectrometer sensitivity was adequate to measure scattered x-rays from a room temperature hydrocarbon foam sample. Initial debris tests were conducted at Z to examine the possibility that debris might damage the laser entrance window in the unique target geometry configuration that x-ray scattering requires. A debris mitigation blast shield was designed and fabricated to help mitigate this possible problem. Scoping studies were performed to verify compatibility between the desired x-ray scattering setup and typical Z dynamic materials and radiation-heated loads. On the theory side, an x-ray scattering code generated by colleagues at Oxford University was obtained and used to predict x-ray scattering signatures from a variety of shock-heated samples. Careful examination of these predictions led to new insight into current challenges facing the worldwide high energy density and warm dense matter communities. Confronting these challenges serves as a focal point for ongoing theoretical research. This combination of

experimental and theoretical research has set the stage for physics advances exploiting this major new measurement capability at Z.

Significance:
This work will advance Sandia's national security mission by expanding its capability to perform dynamic materials and radiation science. Temperature and density measurements of warm dense matter with unprecedented quality would stimulate new innovations in theoretical physics. In addition, the proposed experiments will lay a foundation for future applications to other challenging mission-critical environments. Finally, the community of scientists exposed to high-quality Sandia research will grow, helping ensure continued ability to attract the best staff.

Laser-Based Radiation-Induced Conductivity in Kapton Polyimide Dielectrics at High Dose Rates
148196

Year 2 of 3
Principal Investigator: M. L. McLain

Project Purpose:
The presence of radiation-induced conductivity (RIC) in Kapton polyimide and other dielectric films can have important consequences for electrical components exposed to radiation environments. Previous studies using high-energy electron beam exposures at dose rates up to 10^{10} rad(Si)/s have indicated a Kapton RIC response that is approximately linear with dose rate. For dose rates above 10^{10}rad(Si)/s, it is assumed that the RIC response is also a linear function of dose rate. However, the linearity of the response for higher dose-rate exposures cannot be accurately determined with current linear accelerator or flash x-ray test facilities. Determining the RIC response characteristics of Kapton and other dielectric materials for higher dose-rate exposures will therefore require the development of innovative testing techniques in order to validate model predictions based on lower dose-rate data.

In this project, high-intensity, short-duration laser pulses are used to determine the Kapton RIC response at high dose rates. First-order calculations indicate that dose rates greater than 10^{10} rad(Si)/s can be attained in Kapton with a 532-nm pulsed laser system possessing specific properties. The RIC data obtained in these experiments will verify the linearity of the Kapton RIC response for higher dose-rate exposures, and will ultimately be applied to advanced models for RIC that currently lack high dose-rate experimental validation data. Calculations and device simulations are also being performed to better understand the laser-based results and the existing electron beam results. This approach is novel in that such a method has not been considered for the acquisition of RIC data. Moreover, it appears that a focused study of the photoconductive properties of Kapton as a function of dose rate has not been described in any scientific publication. A key S&T challenge addressed in this project will be the acquisition of radiation effects data without the use of previous testing capabilities.

Summary of Accomplishments:
Two different types of Kapton RIC cells have been fabricated. The first design has an indium tin oxide (ITO) front electrode, and the second design has a "cross-hatch" aluminum front electrode (i.e., has areas without aluminum to allow laser penetration into the underlying Kapton). Each design has an aluminum back electrode. In the initial experiments, we discovered that the output current for the ITO RIC cell exhibits a long relaxation time (i.e., capacitive tail) after the laser pulse ends. Therefore, the "cross-hatch" design is the optimal choice for analyzing the Kapton RIC response. Before conducting the RIC experiments, transmission and damage threshold measurements were completed on each of the samples.

Experiments were planned and conducted using a low-energy flash x-ray (dose rates of ~10^7 rad/s) and two 532-nm pulsed laser systems. The low-energy flash x-ray experiments verified the operation of the RIC cells and provided lower dose-rate data points. The main purpose of the laser experiments was to determine the prompt RIC response of Kapton for higher dose rate exposures. However, we found that the original laser system only provided information on the low dose-rate RIC response because of the low energy per pulse and long duty cycle of the laser. To analyze the prompt conductivity at higher dose rates, we tested the samples using a 532-nm laser system with a 2-ns pulse width and a 200-mJ max energy per pulse. These experiments demonstrated that the high dose-rate RIC response can be obtained using the laser-based technique. The laser-based RIC data is currently being analyzed and compared to previously obtained linear accelerator data at lower dose rates. Physics-based calculations and device simulations are being performed to better understand the RIC response and to correlate the laser energy per pulse to a dose rate.

Significance:

Sandia has many test facilities that expose materials to high-energy ionizing radiation primarily to fulfill Sandia's national security mission. For many radiation-effects applications however, testing capabilities to demonstrate that systems meet requirements are no longer available and/or inadequate. For many radiation effects applications, testing capabilities to demonstrate that systems meet RIC requirements are no longer available and, therefore, predictive capabilities that rely on modeling and experimentation are necessary. However, the ability to obtain accurate data for model development and validation at very high dose rates has been difficult, if not impossible, with current experimental techniques. Success in this project will provide reliable high dose-rate experimental data obtained using a novel laser-based experimental approach. It will also impact the fidelity of advanced RIC models as well as other models used in simulation programs. The experiments performed to date suggest that laser-based RIC measurements are a viable alternative to experiments conducted at linear accelerator (LINAC) or flash x-ray test facilities. From a scientific standpoint, this project could lead to a better understanding of the photoconductive properties of Kapton. For example, the combination of experiments and device simulations could lead to insights on the location of defect levels within Kapton. These results/measurements, to our knowledge, have not been previously published or are not agreed upon in the general scientific community. Given certain defect levels and properties, it may be feasible to develop a novel, as-yet unrealized, dielectric with improved RIC properties.

Fundamental Hydrogen Interactions With Beryllium Surfaces: A Magnetic Fusion Perspective
148957

Year 2 of 3
Principal Investigator: R. Kolasinski

Project Purpose:
The first wall of ITER (originally dubbed the International Thermonuclear Experimental Reactor) will be composed of beryllium. ITER comprises a multinational magnetic fusion experiment that will demonstrate controlled ignition and extended burn of deuterium-tritium plasmas. These beryllium surfaces will be exposed to intense hydrogen plasmas as well as neutrons, conditions that cannot be fully simulated using existing laboratory plasma devices. Furthermore, very few diagnostics are available to characterize how the material reacts to such intense particle bombardment in-situ. Instead, experiments and models that take into account basic processes within the material must be relied upon. The work this project will elucidate is the fundamental processes which underlie the complex plasma interaction with beryllium surfaces, as encountered in a magnetic fusion reactor. We are examining how hydrogen binds to a basic system (e.g., a single crystal Be(0001) surface examined under very controlled conditions) and applying insight gained from this work to a more relevant magnetic fusion environment. Be(0001)+H is particularly interesting from a fundamental surface science perspective because it is a rare example of a low-index, low-Z system which has been sparsely studied. Insights gained from our characterization of this surface can be incorporated into fundamental models of recombination and recycling.

In this project, we are leveraging a unique ion scattering facility at Sandia/California for surface analysis. We will apply novel ion scattering techniques and analysis to reveal the hydrogen adsorbate structure and also to measure the exchange between different isotopes on the surface (publication in *Physical Review B*). One such approach is time of flight spectroscopy, which permits the detection of neutral particles. This improves detection efficiency and avoids corrections for neutralization when modeling scattering experiments. The approach of this project complements ongoing fusion technology missions at Sandia by providing the basic science basis needed to fully understand hydrogen-beryllium interactions.

Summary of Accomplishments:
Our recent progress encompasses both fundamental modeling of ion-surface interactions at grazing incidence and the development of unique surface analysis techniques. Our most significant accomplishment was developing a time of flight system, which involves pulsing an ion beam and using a position sensitive detector to collect backscattered particles from our samples. We found this approach improves the detection sensitivity by a factor of 10^4. We found the detected scattered ion energies to be in accord with theoretical predictions, and more-detailed structural measurements for Be surfaces are presently under way. These enhancements will enable numerous other hydrogen detection experiments relevant to fusion applications.

Definitively determining the binding location of hydrogen on single crystals requires simulating ion focusing along low index directions. Using molecular dynamics, we developed a model that incorporates the physics needed to simulate grazing angle collisions. As a preliminary measure, we have validated these techniques for another system of interest to fusion, W(100)+H, and have submitted a publication to *Physical Review B*. With the modeling approach fully verified on the W(100) system, there are now few obstacles to applying this to simulate scattering on Be(0001).

For detailed analyses of chemisorbed impurities, we added an electron gun that enables us to perform Auger electron spectroscopy. This allows us to examine the effect of impurities on adsorption/desorption processes more precisely during controlled thermal ramps. We were able to perform direct measurements of hydrogen concentration on the surface as a function of temperature. Exchange between hydrogen and deuterium appeared to occur very quickly (nearly instantaneously).

The above work represents solid progress toward proposed milestones, particularly in the areas of modeling and the assembly of the time of flight system, which were pursued more aggressively. We do not foresee any insurmountable obstacles to achieving all of the proposed objectives of this project.

Significance:
From a broad perspective, ensuring that plasma-facing materials can withstand the high particle fluxes encountered in magnetic fusion devices is widely recognized as a pressing technological challenge in fusion research. ITER, a large magnetic fusion experiment now under development, will use beryllium as it primary plasma-facing surface. Our work provides the underlying science needed to model how hydrogen interacts with beryllium, a key priority for the DOE fusion energy science program. With this in mind, this project is important in the context of establishing energy security, given the relevance of fusion as a future energy source.

Because the main emphasis of this work is to foster a better understanding of hydrogen-beryllium interactions, we anticipate many benefits to the broader S&T community. Despite being a technologically important material, many aspects of beryllium behavior when exposed to hydrogen are unknown. Nevertheless, the Be+H is one of the simplest adsorption systems, and therefore is of interest as a model case that can be used to validate the predictions of first-principles codes (such as density functional theory). From this perspective, this work therefore contributes to DOE's mission of basic scientific discovery.

The models developed within this project advance the state of the art for ion scattering and direct recoil spectroscopy simulations, two widely used surface analysis techniques. Since these techniques are unique in their ability to detect hydrogen, the new models will directly benefit the hydrogen in metals and surface science communities. With this work, we demonstrated how direct recoil spectroscopy could be applied to a wide range of adsorbate binding geometries (even for adatoms residing high above the substrate). As a result, the new modeling tools developed enable more sophisticated hydrogen-surface studies.

The new experimental capabilities (time of flight and Auger spectroscopy) added to our scattering spectrometer enable a wealth of hydrogen exchange, recombination, and adsorption experiments. These basic processes are of importance to many Sandia missions, including hydrogen energy infrastructure, hydrogen storage, and magnetic fusion energy.

Low Energy Electron-Photon Transport
151362

Year 1 of 3
Principal Investigator: R. P. Kensek

Project Purpose:
The purpose of this project is to create/develop software to calculate more realistic (i.e., using molecular and/or solid-state effects beyond the independent-atom approach) cross sections (probabilities per path length) for electron/photon radiation transport codes at low energies.

Radiation transport codes are limited by the accuracy of the physics models. General-purpose codes make use of tabulated independent-atom models for the cross sections which are either only evaluated down to about one kilo-electron-volt or extend further with acknowledged large errors (estimated as 1000 percent in solids at the lowest energies). The paradigm shift we propose is to regenerate what would have been tabulated atomic cross sections, but now they include molecular and/or solid-state effects for each material specified. The challenge of this approach is to include these materials properties for each relevant interaction cross section through a reliable numerical technique.

The paradigm shift involves re-generating cross sections for each material, incorporating materials effects (in particular molecular coherent scattering and solid-state effects) as they uniquely affect each element in that particular material. This involves identifying a reliable technique for each change for each relevant electron and photon interaction. For this project, we have identified the relevant cross sections as elastic and inelastic cross sections for each of electrons and photons. FY 2011 concentrated on demonstrating this could be done for photon elastic scattering. FY 2012 will focus on electron elastic scattering while incorporating the new photon elastic-scattering capability into our software Monte Carlo code (ITS), the Integrated TIGER Series of electron/photon radiation-transport codes. FY 2013 will address the inelastic scattering of electrons and photons.

Summary of Accomplishments:

1. We demonstrated successful calculation of a photon coherent cross section for vitreous (amorphous) SiO_2 by using specific structure given through an atomistic "xyz" file (thereby achieving our first milestone). This calculation essentially reversed the data-analysis process used in x-ray diffraction. We also have preliminary results from an approach using a density functional theory (DFT) calculation. Some follow-on work will proceed in FY 2012 to clarify what is now a noisy DFT result. We will demonstrate use of these new cross sections in our ITS (to complete the second planned milestone of FY 2011) and complete the full implementation into our code by Q2 FY 2012.

2. We have had discussions on the challenge of representing amorphous materials with periodic atom models, the need for many atoms, and the resulting challenge for DFT simulations. We have acquired atomic-structure models ("xyz" files) for amorphous SiO_2, a few polymers, and metallic Ni (two models of varying grain sizes). The latter is too large for present DFT calculations.

3. We have acquired and locally compiled a code that can essentially generate our existing electron elastic-scattering cross sections (without atomic structure) by solving the radial Dirac equation. An FY 2012 milestone is to identify and implement changes to introduce atomic-structure effects for the electron elastic-scattering cross section.

4. We described how time-dependent (TD)-DFT could, in principle, completely solve our problem. A practical implementation of this approach is presently impossible.

Significance:
The completion of our first FY 2011 milestone was vital for helping to validate our approach to this project. While, ultimately, this may lead to new capabilities to simulate low-energy electron/photon transport (examples including nanostructures, understanding experiments from low-energy x-ray sources such as Sandia's Z machine and understanding detector energy resolution), it must be recognized this is a first step. This is only for one cross section (photon elastic scattering). Each cross section reveals unique challenges regarding the appropriate way to introduce atomic structure to the calculations.

Even though we have elucidated only one cross section, it is possible that there may be some impact on revisiting a set of (radiation-effects sciences) RES experiments performed in 2004, where an unexplained anomaly was revealed. The x-ray energies were roughly 10 keV. While higher than our target of below 1 keV, it is clear that the cross sections change somewhat just above 1 keV as well (the effects are greater at lower energies). We will examine this issue in forthcoming work.

Modeling Electron Transport in the Presence of Electric and Magnetic Fields
151363

Year 1 of 3
Principal Investigator: W. C. Fan

Project Purpose:
Strategic weapon systems are required to survive the hostile radiation environment produced by nuclear detonations. For example, a potentially large System Generated Electromagnetic Pulse (SGEMP), indirectly generated by radiation, can induce large currents in electrical or electronic components. Existing modeling tools assume that electron transport is totally independent from the electric field created by the deposited charge, which becomes invalid if the field strength becomes large enough to affect electron motion. A related problem is spacecraft charging due to the accumulation of low-energy electrons on the outside surface of a satellite that can cause electrical arcing, breakdown of dielectrics, and eventually lead to the destruction of electronics and failure of mission capability. Current methods for charging predictions oversimplify the relevant physics, such as the dynamic interaction between incident electrons and electric fields generated by deposited charge. With frequent buildup of potentials on the order of 10 kV on spacecraft surfaces, the effect of the high-flux, trapped electrons in the 1–100 keV range could be significant. Current models provide approximate predictions and large safety margins are imposed due to the significant uncertainty.

We will address these issues through modeling and simulation by creating new deterministic algorithms and capabilities for multidimensional electron transport in materials in the presence of electric and electromagnetic (EM) fields. In this project, we intend to adapt many numerical methods commonly used for neutral-particle transport to treat the effects of EM fields on electron transport. These traditional methods may become ineffective or rendered useless since the presence of EM fields creates tight coupling between particle motion and energy, even without collisions. If so, it is necessary to develop new formulation and solution methods to address these issues, thus making this project extremely challenging.

Summary of Accomplishments:
We have developed a mathematical model to include the effects of the Lorentz force on electron motion into the Boltzmann equation. These effects are described by a gradient of momentum change in the velocity space, which leads to several differential operators characterizing the continuous changes in energy and directions of electrons under the influence of EM fields. Surprisingly, these operators can be cast into operator forms similar to those in the Fokker-Planck approximation, such as the continuous-slowing-down (CSD) and momentum transfer operators, commonly used to model electron transport. These similarities allow us to experiment many established discretization and solution methods in the current research.

We have applied the discontinuous finite-element method (DFEM) in space and energy to discretize terms involving the spatial and energy derivatives, respectively. This may be the first time a generalized DFEM in energy is applied to radiation transport, but may be required to accurately treat the redistribution of electron energy due to the electric field. It is worth noting that this approach can also improve upon how the continuous-slowing-down operator is discretized and should provide higher-order accuracy to the existing electron transport capability.

In addition, we have implemented the vector-based finite elements, where the degrees of freedom are assigned to the edges rather than to the nodes of the elements, into the radiation transport framework SCEPTRE to represent the EM fields. These classes of finite elements have been used successfully in many unstructured electromagnetic solver packages. We have also implemented the core electromagnetic solver from EMPHASIS directly into the radiation transport solver to expedite the current research by bypassing complications in data transfer between codes.

Significance:
Our accomplishments in FY 2011 have established a solid foundation to the proposed works in the next two years: we will be able to rapidly implement and test many conventional discretization and solution algorithms, explore advanced numerical schemes, and produce a software package to model electron transport with electromagnetic fields.

Successful completion of this project will yield a computational tool to model electron transport with externally applied and/or self-generated electromagnetic fields. This capability would benefit current Sandia missions involving radiation effects on weapons, satellites, and missile defense systems from both hostile and natural radiation environments. Expanded simulation capabilities would also improve Sandia's ability to meet the needs of future collaborators in the defense, homeland security, and aerospace communities. This unique resource will help preserve and expand Sandia's national leadership in the area of radiation transport and radiation effects.

Mesoscale Modeling of Dynamic Loading of Heterogeneous Materials
151364

Year 1 of 3
Principal Investigator: J. Robbins

Project Purpose:
The purpose of this project is to develop an advanced modeling capability to simulate the dynamic response of heterogeneous materials. Material response to dynamic loading is often dominated by microstructure (grain structure, porosity, inclusions, defects). An example important to Sandia's mission is dynamic strength of polycrystalline metals where heterogeneities lead to localization of deformation and loss of shear strength. Microstructural effects are of broad importance to the scientific community and several institutions within DoD and DOE; however, current models rely on inaccurate assumptions about mechanisms at the subcontinuum or mesoscale. Consequently, there is a need for accurate and robust methods for modeling heterogeneous material response at this lower length scale.

A mesoscale modeling capability would serve two essential roles. The first is to simulate, in full detail, the response of polycrystalline material to dynamic loading. In this case, the microstructural details appear explicitly in the simulation. This approach is computationally expensive (days on a supercomputer), but provides direct insight into the microstructural origins of material response. The second role, with potentially broader impact, is to inform lightweight (minutes on a desktop computer) continuum models with information from mesoscale simulations. At longer length scales, where direct numerical simulation (DNS) of microstructural effects is not computationally feasible, "upscaling" techniques are a proven approach. Unfortunately, these methods typically assume static equilibrium, making them inappropriate for our applications. Further, current upscaling methods do not leverage statistical information about material response made available through mesoscale calculations. This project will address these problems using Sandia's unique computational capabilities and codes to perform DNS of a statistically significant number of microstructure realizations. Results will inform development of much-needed dynamic upscaling models.

Summary of Accomplishments:
We have made the following progress:

Direct Numerical Simulation (DNS):

- Generated representative microstructures based on 1) Monte Carlo simulation of grain growth and 2) standard Voronoi approximations, and implemented a method for initialization of microstructural information in Arbitrary-Lagrangian-Eulerian General Research Applications (ALEGRA).
- Implemented anisotropic elastic constitutive model in ALEGRA and performed large scale DNS of dynamic response of polycrystalline Nickel to ramp loading. Initial results confirm that the local deformation state is highly nonuniform and multidimensional even under "uniaxial strain" loading conditions.
- Implemented a rate-dependent microplasticity model in ALEGRA that will be used to simulate the strength behavior spatially resolved heterogeneous metals.

Reduced Degree of Freedom (DOF) Models:

- Higher-order model equations for conservation of momentum (micro-inertia model) have been implemented in Laslo to account for local inhomogeneities that would otherwise be ignored in continuum calculations. Micro-inertial constitutive parameters were determined from DNS of spatially resolved polycrystalline samples. Evaluation of model efficacy is under way.

- The perturbation finite element method (PFEM) and Monte Carlo (MC) method have been implemented in Laslo to enable quantification and propagation of uncertainty arising from projection from DNS to reduced DOF models. These models take statistical data from DNS in the form of mean, variance, and auto-correlation to account for spatial variation of material response. The PFEM and MC methods have been used to quantify the uncertainty in response arising from random grain structure in Nickel and Aluminum. Initial results clearly demonstrate the importance of accounting for material heterogeneity, particularly in loading regimes where material strength is significant.
- Implemented Mindlin elasticity for the purposes of analyzing dispersion behavior and evaluating the method for application to dynamic loading of heterogeneous materials without spatially resolving the material microstructure.

Significance:
Sandia has considerable investment and commitments in several national missions involving prediction of material response under extreme conditions. Examples include dynamic experiments and material model development supporting the NNSA Weapon Science Campaigns, and research to support the joint DoD/DOE Munitions Program to develop advanced armor, armor penetrators and energetic munitions. Successful achievement of these goals will require inclusion of material heterogeneities at the mesoscale for accurate predictions and significant effort is already invested in these efforts. Success of the proposed research will provide a unique capability to explicitly treat natural material variations and give our project a differentiating advantage. Specifically, this project is addressing the impact of grain-scale effects through advanced modeling techniques. In addition to providing modeling capabilities, both for direct numerical simulation microstructurally informed desktop computation, we will also elucidate the connection between mesoscale features and uncertainties in experimentally measured parameters. Hence, the contributions of this work will include 1) improved understanding of the complex physical response of polycrystalline materials and 2) a range of computational tools to facilitate accurate modeling of a range of materials of interest.

The tools developed thus far make it possible to begin developing the higher order (low-DOF) constitutive models that will ultimately be the mathematical support for microstructural information from direct numerical simulation (DNS). In the classical continuum setting, the material response is introduced through the constitutive relationship between a pair of work conjugates, typically stress and strain. In microcontinuum theory, however, a richer characterization of the material behavior is possible due to the simultaneous presence of multiple conjugate pairs. For example, in Mindlin theory those are cauchy stress — macro-strain, relative stress, relative strain, and couple stress — microdeformation gradients. These constitutive relationships are currently under development.

The new DNS capabilities (e.g., spatially resolved representative microstructure and microplasticity constitutive model) provide the means whereby the material parameters for these higher-order relationships will be computed. Specifically, DNS will be used to compute the response of spatially resolved polycrystalline metals to dynamic loading. Results from these very highly resolved simulations will be used to extract the constants that reduce the error between the low-order / high-DOF and high-order / low-DOF results.

This minimization of error is effectively a projection between model representations, making it possible to quantify the error that is introduced and to determine a statistical uncertainty of the low-order constants. In addition to the higher order models and DNS capability, methods to propagate uncertainty through transient simulations have been implemented and tested. The net result of this capability is a desktop simulation that runs in a matter of minutes, implicitly accounts for the effects of material microstructure, and explicitly provides the uncertainty in output.

Dynamic Temperature Measurements with Embedded Optical Sensors
151365

Year 1 of 3
Principal Investigator: D. H. Dolan III

Project Purpose:
Dynamic compression experiments provide unique insight into material behavior under extreme conditions. To fully utilize these experiments in equation of state and phase diagram studies, temperature measurements are needed in the compressed state. Despite years of effort, dynamic temperature measurements are generally considered unreliable. This skepticism is largely due to problems with dynamic optical pyrometry. Pyrometry is challenging in dynamic compression experiments, and its interpretation requires additional information (e.g., sample emissivity). Modest temperatures (<1000 K) characteristic of ramp wave compression are extremely difficult to measure with pyrometry. Existing alternatives to pyrometry, such as Stokes/anti-Stokes Raman spectroscopy and neutron resonance spectroscopy, are either too material-specific for general use or require special facility capabilities.

We are developing embedded sensors that will allow accurate temperature measurements under dynamic compression. These sensors will be based on optical property changes that can be correlated to temperature. For example, the reflectivity of gold in the visible spectrum is known to vary with temperature, exhibiting increasing reflectivity in the blue region and decreasing reflectivity in the red region with increasing temperature. By measuring changes in the visible reflectivity of an embedded gold film, it should be possible to extract temperature information in a dynamic compression experiment.

This project merges benefits of embedded sensors with optical spectroscopy, a new approach in the quest for dynamic temperature measurements. Separating temperature and compression effects in these sensors, both experimentally and theoretically, is the primary challenge of this project—a quite difficult task. Temperature measurements will always be difficult, but if successful, embedded optical sensors may overcome many of the practical difficulties that hinder other approaches. If successful, temperature measurements may become a standard part of dynamic compression research.

Summary of Accomplishments:
Several improvements were made to the time-resolved reflectivity diagnostic. Foremost among these was the discovery of the "MegaSun" light source, which produces intense flashes with a smooth emission spectrum. The source was obtained from the Nevada Test Site and moved to Sandia earlier this year. Performance characterization of the streaked spectroscopy system is under way.

Heated ellipsometry measurements were performed on the sputtered gold films produced at Sandia. Basic spectral trends for heated gold described in the literature (increased reflectance in the blue, decreased reflectance in the red) were observed; minor differences in the reflectivity were found, but this is typical for different sample preparations. Thermal cycling was found to be an issue: samples heated to 75 °C, 150 °C, and 275 °C did not exhibit their original reflectivity when cooled back to room temperature. We found that annealing at 250 °C for 4+ hours makes sputtered gold films (300 nm thick) stable to thermal cycling. Ellipsometry measurements are currently limited to temperatures of 300 °C, but a new capability will be coming online shortly to reach temperatures of 600 °C.

Gold reflectivity measurements were also performed in diamond anvil cell experiments at the Advanced Photon Source. When combined with resistive heating, this allowed us to study the changes of reflectivity for temperatures up to 500 °C and pressures of 20 GPa. Reflectivity trends were consistent with heating at zero pressure, and though compression produces effects similar to heating, it is accompanied by spectral changes not found during isobaric heating.

Phenomenological reduction of the measurements described above is under way to develop methods of extracting temperature and pressure from a gold reflectivity measurement. An empirical dielectric model for gold is also under development that will tie observed changes to intraband and interband effects in the dielectric function.

Significance:
Development of a reliable temperature diagnostic has enormous impact throughout dynamic compression research. Accurate temperature measurements are crucial to equation of state development and are needed for mapping phase boundaries. Fundamental questions, such as the extent to which ramp-wave compression is isentropic, cannot be answered without temperature measurements. The purpose of this project is to provide a new method for measuring dynamic temperature states, in alignment with DOE goals for scientific discovery and innovation.

Dynamic temperature measurements based optical reflectivity changes offer two benefits to the study of extreme environments. First, reflectivity-based measurements can potentially probe modest temperature states (<1000 K) where more established techniques, such as optical pyrometry, are infeasible. For intermediate temperatures (1000–2000 K), reflectivity measurements may help validate pyrometry diagnostics, reducing the substantial uncertainty associated with dynamic temperature measurements.

Even if temperature cannot be unambiguously derived from reflectivity changes in an embedded optical sensor, the development of time-resolved reflectivity has other benefits in dynamic compression research. Phase transitions, both solid-solid and solid-liquid, could be detected via changes in the reflected optical spectrum. Dynamic thicknesses of transparent media (hydrogen, water, etc.) might also be discernible through optical reflectivity measurements.

Spectral Line-Broadening in White Dwarf Photospheres
151366

Year 1 of 3
Principal Investigator: G. A. Rochau

Project Purpose:
White Dwarf (WD) stars are potentially the most accurate independent chronometers for constraining the ages of the Galactic disk, halo, and star clusters, and provide a lower limit to the age of the universe. This accuracy depends on stellar evolution models benchmarked against observational data on WD properties: mass and surface temperature. The primary method to determine these properties is through comparison of observed optical line profiles to synthetic spectra from theoretical atmosphere models, adjusting the assumed mass and temperature to obtain the best fit. Understanding the line profiles and how they relate to the plasma conditions is of significant importance to the precise and accurate determination of the WD properties and their inferred ages. The stellar masses inferred from this spectroscopic method, however, disagree with recent gravitational redshift measurements. In addition, the spectral analysis breaks down completely at low surface temperatures. Inaccuracy in the line-shape theory is the leading hypothesis for this breakdown at plasma conditions that span T_e = 0.3–5 eV and $n_e = 10^{(16–18)}$ cm^{-3}.

In this project, we are testing the line-shape theory by accurately measuring the emergent line profiles from well-characterized hydrogen plasmas heated to WD conditions by the ~1 MJ of x-rays produced on the Z machine. Testing the line-shape theory at these densities requires the creation of a large volume of plasma with very uniform conditions in order to achieve the optical depths necessary to measure the full line profile. These are the first line-shape experiments to utilize purely x-ray heated plasmas and the first to use multi-cm scale samples. Benefits include minimum turbulence and independent control of the plasma density, heating flux, and optical depths. The successful development of this platform will address the WD problem and can be expanded to address molecular effects at low electron temperature, effects of elemental mixtures on line shapes, and effects of correlations in the warm dense matter regime.

Summary of Accomplishments:
Work in FY 2011 focused on two main activities: 1) Developing a radiation-hydrodynamics model for designing gas cells on the Z facility and 2) Testing the gas-cell designs on Z using time-resolved optical spectroscopy to infer the approximate plasma conditions and observe the resulting line profiles. Both of these activities were highly successful. The baseline design uses a cylindrical gas cell with gold walls that is 6 cm long and 2 cm in diameter, placed 35 cm from the axis of a z-pinch dynamic hohlraum (ZPDH) radiation source. The optical spectra are observed along the length of the cell, perpendicular to the direction of the heating radiation from the z pinch. The gas cell has a 1.5-micron-thick Mylar window to both contain the gas and allow the z-pinch x-rays to enter the cell. Rad-hydro simulations indicate that this Mylar window has a profound effect on the heating of the gas. If the cell is filled with H, the large optical depths of the Mylar above the H photoionization edge prevent the gas from being heated directly by the z pinch. Instead, the H gas is primarily heated by radiation absorbed and re-emitted from the Au cell walls. Both the simulations and the experiments indicate that 15 Torr of H gas only reaches temperatures of ~1 eV, but stays at this temperature for a few-hundred ns due to both the long decay of the wall temperature and the low emission opacity of the H. This is a very relevant condition to WD photospheres. The measured line-profiles of the Balmer H-beta line at these conditions are in good agreement with previously published measurements. Extending the measurements to Balmer lines with upper levels of n> 4, higher densities, and lower temperatures will provide a more stringent test of the line-shape models.

Significance:
The disagreement between the WD masses determined either by spectroscopic fits or through the gravitation red-shift is an indicator that something may be fundamentally wrong with our understanding of how atoms behave when immersed in a plasma. In particular, we may not understand the details of how the plasma microfields affect the bound electrons at high electron density and low temperature. There is little data in the literature to benchmark calculations of this type, and there is no data that can sufficiently address the very complex issues surrounding electron energy levels that begin to overlap with each other and the unbound continuum due to perturbations by the microfields. Therefore, the successful outcome of this project will provide benchmark data on fundamental atomic processes in plasmas. This work is applicable not only to the WD problem, but also to such fundamental issues as continuum lowering in high density plasmas and the subsequent effect on the ionization balance.

In addition to the impact on the understanding of atoms in plasmas, this work will also advance the DOE strategic theme of scientific discovery and innovation by expanding the capability to use the Z facility for fundamental radiation science, a growth area for all high energy density (HED) facilities across the NNSA complex. Line shape measurements with unprecedented quality would stimulate new innovations in theoretical physics and expand the community of scientists exposed to high quality Sandia research. The research is also leveraging an academic partnership with the University of Texas, leading to more basic research using Z and the training of graduate and undergraduate students in HED science.

Z-Petawatt Driven Ion Beam Radiography Development
151367

Year 1 of 3
Principal Investigator: M. Schollmeier

Project Purpose:
In this project, we will seek to perform laser-driven ion beam radiography of an object during a megaJoule-driven discharge of the Z machine in order to measure the object's electromagnetic field distribution. This will allow unmatched insights into both the target performance for spherical capsule implosions, magnetic flux compression or astrophysical jet simulations, as well as the machine performance by mapping the magnetic field distribution with micron spatial resolution. Because of the high magnetic fields and the tremendous amount of x-ray energy created during a discharge, this approach is scientifically and technically very challenging. Required is the capability of creating high ion beam energies (10-100 MeV range) with a short-pulse, high-energy laser system providing intensities well above 1020 W/cm^2. The Z-Petawatt laser (ZPW) demonstrated its readiness for x-ray backlighting in April of this year, and it can be modified to utilize ion acceleration at the Z machine by using novel, plasma mirror focusing devices.

Although ZPW demonstrated its capability as a driver for x-ray backlighting, its application to drive ion acceleration on the Z machine requires orders of magnitude higher laser intensities than currently possible, and a beam deflection by a plasma mirror. Our approach is to address both issues simultaneously by using an ellipsoidal plasma mirror, provided it survives long enough in the violent environment of Z machine's discharge. A successful proton beam radiograph would create a whole new diagnostic capability, potentially having impact on Sandia's involvement in the National Ignition Campaign as well as on pulsed-power driven physics in general. The higher magnetic rigidity of heavy ions compared to protons motivates the development of heavy-ion beam radiography, which has never been demonstrated before. Electromagnetic field mapping of the fields created by capsule implosions, compressed magnetic fluxes, or magnetized astrophysical jets will enable unprecedented insights into the underlying physics.

Summary of Accomplishments:
In our first year, we focused on better understanding the ion source. We found, experimentally, that a reduction of the target volume increases both proton yield and maximum energy. Compared to millimeter-sized thin foil targets, maximum energies and yields from these so-called Mass-Limited Targets (MLT) scale differently with thickness. An experiment was performed at the Trident Laser Facility at Los Alamos National Laboratory to clarify this scaling. During this experiment, a new proton energy world record of 75.4 MeV was set, using our MLT. We found that effects from the picosecond prepulse of the laser cause the ion source to deteriorate prior to the main pulse arrival. This effect has not been seen in simulations before, pointing to missing details in the models. Further theoretical and numerical investigations are ongoing; a publication is in preparation. We also did a ride-along experiment on the Z machine with the Compact Point-Projection System to measure the background of the proposed ion beam detectors—it was found to be negligible. Two- and three-dimensional particle-in-cell simulations have been performed to understand the experimental MLT findings, and to achieve a detailed insight into the ion acceleration dynamics at the source. A large-scale, 3D particle-in-cell simulation has been performed using the supercomputer at the New Mexico Computer Applications Center; data analysis will lead to a reduced model of laser-ion acceleration that can describe the six-dimensional phase space of the ion beam. In collaboration with Raytheon K Tech's Materials Processing and Coatings Lab (MPCL) we have developed a conceptual prototype of a novel, alignment-free ellipsoidal plasma mirror device for enhanced proton acceleration, improved laser

pointing stability, and debris mitigation. Our collaboration with the Institute for Fusion Studies at the University of Texas at Austin resulted in a better understanding of electron acceleration in preplasma via parametric resonance. A publication will be submitted soon.

Significance:

This project should significantly improve the capability of the existing Z-Petawatt laser to provide fundamental new insights into a variety of magneto-hydrodynamic phenomena. The ability to measure electromagnetic fields at a radiating z-pinch load would be a breakthrough, allowing rapid progress in the understanding of important target physics and is relevant to the Sandia's role in the National Ignition Campaign, DOE's strategic needs in nuclear weapons stewardship and energy security. This ability would also improve the capacity of existing facilities for enhanced-capability scientific research.

New Strategies for Pulsed Power Transmission Lines: From Repetitive to Replaceable to Recyclable
154060

Year 1 of 3
Principal Investigator: M. E. Cuneo

Project Purpose:
The most obvious barrier to the use of pulsed power for inertial fusion energy (IFE) is the need to have a conducting path for the current between the driver and the target, and to create this path repetitively. Previous LDRD research suggested the Recyclable-Transmission-Line (TL) as the most promising approach for repetitive driver-load coupling for high fusion yields. The purpose of this project is to develop a small-scale proof-of-principal recyclable transmission line system for automated replacement of transmission lines in a small-scale pulsed power driver. We will also study the appropriate materials to be used for transmission lines, compatible with fusion energy systems. Finally, repetitive conditioning of transmission lines will also be studied and may lead to new regimes of operation for pulsed power systems. The sequence of research proceeds from “Repetitive”-TLs to “Replaceable”-TLqqs and will be relevant to “Recyclable”-TL operation.

Summary of Accomplishments:
1. We developed an animated conceptual model to repetitively stage, evacuate to high vacuum, insert, fire the pulsed power system, and extract a transmission line diode within a self-contained and fully automated system.
2. We developed a preliminary concept for the fast annular valve. The fast annular valve is a crucial component to the integrated system as a method to isolate the majority of the system volume, to maintain a constant vacuum and to isolate the driver from the debris produced during a pulse. The purpose of maintaining vacuum has been established as a prerequisite for enabling repetitive replacement of transmission line inserts.
3. We developed a preliminary concept for the primary transmission line insert mechanism. The transmission line insert is crucial to the integrated system because it is the mechanism that enables fast repetitive insertion, firing of pulsed power system, and extraction of the diode within the automated system.
4. We developed an experiment with the University of Michigan to test the repetitive conditioning of transmission lines with repetitive pulsed power, at vacuum pressures of 10^{-5} to 10^{-7} Torr, repetition-rates of 0.1 Hz, and anode-cathode gaps of 2 to 4 mm.
5. We are developing fusion nuclear science models of neutron shielding and tritium breeding with the University of Wisconsin to select the appropriate first wall and alternate transmission line materials.

Significance:
This project has relevance to scientific discovery and innovation in pulsed power science and technology, and in pulsed power fusion. Automated handling and replacement of transmission lines will be a required aspect of any pulsed power facility at higher outputs than Z (> 30 MA), even for single shots, in particular for facilities that generate high fusion yields. Handling of high fusion yields, even for single-shot systems, will require methods for shielding the facility. This project enables progress on integrated pulsed power driver and target designs to handle high yields with low activation. The project is also relevant to energy security, environmental responsibility, and national security in laying a foundation for inertial fusion energy applications of pulsed power. Finally the project has applications to nuclear security in possible relevance to aspects of radiation effects.

Integration of MHD Load Models with Detailed Circuit Representations of Pulsed Power Drivers
155458

Year 1 of 3
Principal Investigator: C. Jennings

Project Purpose:
State of the art magnetohydrodynamic (MHD) models of loads fielded on the Z accelerator are typically driven by reduced, or simplified circuit representations of the generator, while generator models typically couple to simplified representations of the load. The performance of many of the imploding loads is dependent on the current and power delivered to them and, therefore, may be strongly influenced by the generator's response to the rising inductance of these loads. Current losses diagnosed in the transmission lines approaching the load are further known to limit the energy delivery, while exhibiting some load dependence. Studying the efficiency with which power may be coupled between the generator and the load in this implicitly linked, rapidly evolving system therefore necessitates the integration of detailed generator and load models. This project will develop an integrated load-generator model to establish a predictive capability that may be used to both explore how existing and next-generation pulsed power drivers may be optimized to support specific loads, and how loads may be better optimized to the specific response of the generator.

Summary of Accomplishments:
Electrical data for a large number of shots from K-shell source and dynamic hohlraum loads has been processed and analyzed to calculate convolute current loss terms. K-shell sources typically have short implosion times at high velocities developing very high load voltages, whereas the implosion of dynamic hohlraum loads is typically much slower, with a lower voltage developed at stagnation. Analysis of these data sets has, therefore, enabled convolute losses to be calculated over a wide range of load voltage histories. This analysis has been extended to smaller diameter beryllium liner loads, with load calculations performed to assess the simulated distribution of current during implosion, to check consistency between load calculations and generator electrical diagnostics, so that this intrinsically simpler load configuration may be used to study generator load coupling.

Load calculations of large-diameter wire array loads have been performed, constraining the voltage developed by the imploding load to not exceed the voltage measured by machine diagnostics. This has allowed secondary current loss terms to be calculated from the resulting difference between measured and calculated currents between the convolute and the load. This analysis has been repeated for multiple shots allowing an average loss term to be determined for application within a circuit model. Further studies have been conducted investigating how the location of current losses in the vicinity of the load affects energy delivered to the load at stagnation, by varying the magnetic energy available to it. Characterizing these loss terms, and understanding the sensitivity of load performance to the placement of these losses is a prerequisite for the ongoing efforts to integrate a load and generator model.

Significance:
This work is relevant to DOE/NNSA strategic needs in nuclear weapons stewardship. The work would potentially support nuclear weapons stewardship by increasing the x-ray load yields for weapons physics and effects certification experiments and by allowing higher pressures and more flexible loading paths on dynamic materials experiments. If successful, it would also support energy security by increasing the efficiency and decreasing the cost of inertial fusion energy sources. The work improves the capacity of existing facilities for high-quality scientific research by developing a predictive modeling capability that could allow us to design new pulsed power facilities and experiments.

Flyer-Plate-Driven Hydrodynamic Instabilities Using Z
156252

Year 1 of 3
Principal Investigator: E. Harding

Project Purpose:
Hydrodynamic instabilities such as Richtmyer-Meshkov (RM), Rayleigh-Taylor (RT), and Kelvin-Helmholtz drive the mixing of fluids, including hot, dense plasma. In the context of laboratory fusion, the detailed growth and evolution of these instabilities is studied in order to better understand their effects on energy yield. Previous plasma experiments used lasers to produce systems where these instabilities grew. In this project, we will develop a novel experiment that will generate RM and RT instabilities using the impact of a flyer plate launched by the Z machine. The flyer plate is essentially a high-velocity piece of aluminum that replaces the laser as the energy source. The flyer-plate approach has several advantages over the previous laser experiments—primarily, the flyer plate has enough energy to drive a relatively large, steady state flow of plasma. In this configuration, the nonlinear growth regime of these instabilities, and possibly a fully turbulent state, should be easily accessible for the first time.

This effort represents the first attempt to generate and image hydrodynamic instabilities using a flyer-plate system on the Z machine. This novel experimental configuration will require making several existing capabilities of the Z machine compatible for the first time. Combining these capabilities entails considerable risk, yet if successful, the experiment will access new regimes that were not attainable in previous experiments. The data from these experiments will not only be especially interesting from a basic science perspective, but will also be useful for benchmarking many of the modern hydrodynamic computer codes.

Summary of Accomplishments:
We now have 2D Arbitrary-Lagrangian-Eulerian General Research Applications (ALEGRA) simulations of planar and cylindrically converging RM instabilities. The cylindrical simulations show that it is possible to measure a growing RM instability on the inside surface of a foam-filled cylindrical shell made from Be. This was accomplished by using a thin, Al coating on the inside surface of the shell. Due to its higher opacity, the Al shows up well in x-ray images, and delineates the interface between the Be and foam. Nevertheless, the planar case appears to be easier to diagnose, thus providing a more accurate measurement of the RM growth. We have begun collaborating with the Naval Research Laboratory, Washington, D.C., and the University of Castilla-La Mancha, Spain. Our collaborators will be developing the linear RM theory that will include a non-ideal gas equation of state, and nonlinear theory to help us better understand the time-dependent growth of the RM instability. For the planar experiment, we worked with General Atomics, Inc. and Brush-Wellman, Inc. to develop a new Cu-doped (5% by atom number) Be alloy that will help us fabricate a planar target with a high-opacity tracer layer. We have also learned that the planar geometry will be extremely useful for carrying out RT and Kelvin-Helmholtz experiments. These experiments can be used to create a system where two instabilities are acting simultaneously. The theory for these dual instability systems has not yet been developed.

Significance:
An understanding of the mixing driven by the Richtmyer-Meshkov, Rayleigh-Taylor, and Kelvin-Helmholtz instabilities is important to the success of the inertial confinement fusion (ICF) program. The experimental aspect of this project will provide a stringent test of modern simulation codes. These codes must accurately predict the growth of these instabilities in imploding fuel capsules in order to correctly calculate the energy output. These experiments will also help validate the assumptions

of the previous laser experiments that were performed in support of the ICF program. Furthermore, the ICF community is currently interested in the resistance to deformation (sometimes referred to as "strength") of various materials at high temperature and pressure. If successful, it is very likely that the experiments in this project will enable us to make strength measurements that are valuable to the ICF community.

Kinetics of Radiation-Driven Phase Transformations in PZT Ceramics
157693

Year 1 of 3
Principal Investigator: N. W. Moore

Project Purpose:
Understanding phase kinetics in ferroelectric ceramics is of broad scientific and technical interest. An unknown parameter is the kinetics of phase transformation of lead zirconate titanate (PZT) ceramics following rapid heating. On heating from room temperature, PZT transforms from a ferroelectric phase (FR1) to a less polarizable one (FR2), and finally to a paraelectric phase (P) where it can no longer hold stored charge. The kinetics of these transformations is thus strongly coupled to the material's ability to function as a ferroelectric under rapid heating.

The only phase kinetics yet measured for PZT are those driven mechanically or electrically along the pressure axis of the phase diagram. Because kinetics along the temperature axis is unexplored, the phase trajectory following rapid heating is also unknown. A key exploratory aspect is that optical diagnostics suitable for observing this trajectory in PZT have not been attempted. In particular, structural similarities produce considerable risk in differentiating the rhombohedral FR1 and FR2 phases. This work presents unique opportunities to clarify these differences. The kinetic mechanisms and resulting thermomechanical response can then be fully explored. Phase dynamics are of broad scientific and engineering importance, yet are poorly understood for many materials, including PZT. For example, complexities may arise involving shear stresses created by thermomechanical shock, radiation-induced defects, or metastable phases. Such discoveries will make both short and long-term contributions to multiple missions in the pure and applied sciences.

Summary of Accomplishments:
A high-temperature polarimeter has been designed, fabricated, and assembled to allow for evaluation of optical diagnostics based on circular/linear birefringence and dichroism believed to be suitable for nanosecond determination of phase kinetics in La-doped PZT (PLZT) ceramics in response to rapid heating through pulsed irradiation. In addition to the optical train, this involved engineering a rotatable annular sample heater capable of ± 0.5 °C control and uniformity over a range of 500 °C, as well as operability in a pulsed-radiation environment. In addition, coupled electron-photon transport calculations have been completed to quantify requirements for the optical diagnostic sensitivity, temperature control, radiation dosing, and sample characteristics.

Significance:
The dynamics of phase transformation and atomic-scale processes is at the cutting edge of modern materials science, and is also consistent with DOE's ongoing investment in radiation effects sciences, including radiation effects research at Sandia. Additionally, it is consonant with the DOE strategic themes of nuclear security and scientific discovery / innovation.

Laser-Ablated Active Doping Technique for Visible Spectroscopy Measurements on Z
158701

Year 1 of 3
Principal Investigator: M. R. Gomez

Project Purpose:
Spectroscopic measurements can reveal information about plasma parameters that would be otherwise extremely difficult to determine. In many cases, the spectroscopic systems observe a region of the plasma that contains sharp gradients in the plasma parameters, which obscures the intended measurement. The effect of these gradients can be minimized by incorporating a localized dopant within a relatively constant region of the plasma, and observing emission from the dopant. One goal of this project is to create an active doping system for use with the Streaked Visible Spectroscopy (SVS) system on Z. This new capability will be particularly useful in diagnosing the plasma formation and evolution in the post-hole convolute on Z. The intense electric and magnetic fields in the convolute create an interesting plasma environment. Spectroscopic measurements of the plasma in this region may show significant Stark shifting and Zeeman splitting, as well as Stark Broadening and possible Doppler shifting. Few spectroscopic measurements have been made of plasma under such extreme conditions due to the complicated nature of the measurements. With the active doping system, such measurements will become more feasible.

In this project, we are developing a new “active doping” capability for use with the SVS system on the Z Machine. In this technique, a low-density contaminant with favorable spectroscopic characteristics is intentionally inserted into the system to monitor plasma conditions. This capability will require development of a fiber-coupled laser system, design of new electrode hardware, and establishing a new triggering setup for Z. The new system will advance a number of projects that utilize the visible spectroscopy diagnostic on Z. Primarily, we are interested in utilizing active doping to make highly spatially resolved measurements of the plasma within the post-hole convolute. The active doping capability could also be used to make independent temperature and density measurements of the plasma in the White Dwarf Photosphere Experiment.

Summary of Accomplishments:
- Established streaked visible spectroscopy diagnostic at location required for these experiments
- Selected laser for active ablation of dopant material
- Completed preliminary design for fiber-optic-coupled, high-spatial-resolution, high-collection-efficiency diagnostic probe
- Started development of MatLab script for processing visible spectroscopy data
- Completed redesign of diagnostic coupling. Increased signal-to-noise by approximately 3x.

Significance:
This research is relevant to the DOE Mission, Scientific Breakthroughs. Specifically, this research will be useful in determining the feasibility of pulsed power-driven fusion energy. This capability will enhance the diagnostic suite available for use on Z. One application for this capability is diagnosing the plasma in the post-hole convolute. The leading pulsed power-driven inertial fusion energy concepts utilize a convolute, thus its performance is of particular interest. Knowledge of the convolute plasma evolution and its association with current loss will provide insight as to what should be the optimal design for future iterations of the convolute.

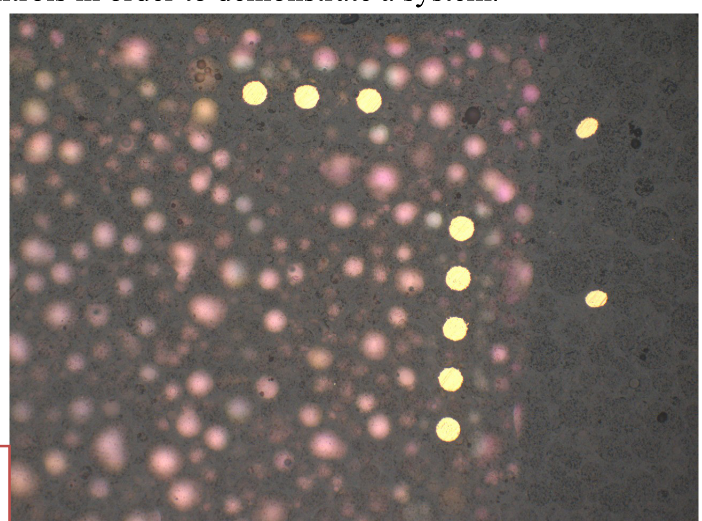
DEFENSE SYSTEMS AND ASSESSMENTS INVESTMENT AREA

This investment area funds both fundamental and applied research into science and technology that is or can be rendered applicable to national defense — from software to assist the human intelligence analyst by filtering and more-coherently organizing intelligence streams, to virtual training scenarios for analysts and warfighters to a variety of improved detection-science and -technology solutions for chemical and biological threats to populations, and even to improved robotic agents to mitigate risks to soldiers and civilians in dangerous scenarios. Through these and other initiatives, projects in this investment area contribute to national defense and homeland security — and therefore, help diminish the global threat of terrorism.

Packaged Integrated Thin Sensor
Project 141605

This project is producing a functioning sensor prototype that combines power, electronics, packaging, circuit board, and sensors into an integrated very thin platform. The intent is to demonstrate the capability to fabricate a system that retains functionality under the extreme conditions at which subcomponents are processed and packaged. Previous efforts in this area have been plagued power-source issues, problems with the electrical interconnects between the circuit board and the die function, and with design and fabrication of sensor-specific ancillary electronics that need to be included in the device. The integration is not trivial, and requires significant advancement in the state of the art in interconnects, power sources, and sensor controls in order to demonstrate a system.

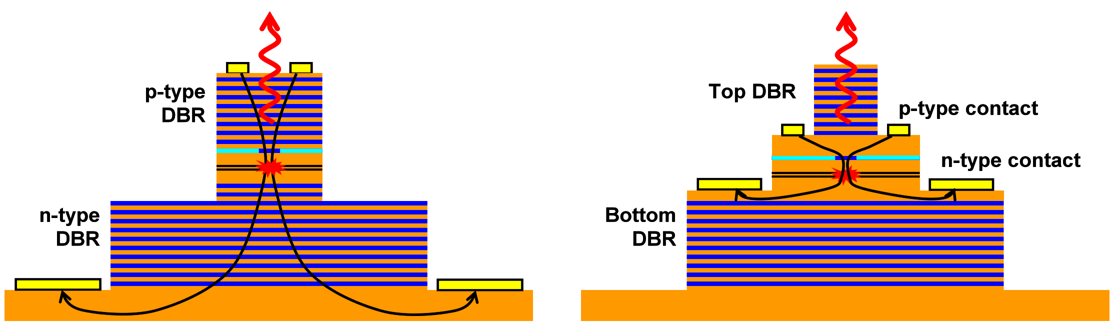
Such a system promises improved reliability and enhanced functionality for national security mission space. Each of the technology areas being integrated helps enhance the skillset of available technologies for nuclear weapons and national defense customers and tools developed in this project become the backbone of a technology trade-space in "things thin."



The team is currently working through the issue of where to stop the device processing to provide the best opportunity to make interconnections. This micrograph shows contacts revealed upon die processing. Each pad is 25µm wide, with approximately 40µm between pads. Interconnects to this die layout are the biggest project challenge.

Cryogenic FPA Optical Interconnects
Project 151269

In the interests of projected upcoming needs in satellite technology, this project is developing optical circuitry that will function cryogenically. Next-generation satellite-based imaging systems will require focal plane arrays (FPAs) with higher pixel number and faster frame rates, driving the need for higher-bandwidth data interconnects to transfer data from the FPA. Optical fiber interconnects have numerous advantages over electronic connections, including scalable bandwidth and reduced size, weight and power consumption (10x reduction) compared to electrical interconnects. But numerous new technology elements will be required to accomplish this goal, and this project's team is approaching these novel technologies, including cryogenically functioning vertical cavity surface emitting lasers (VCSELs)



Standard VCSEL (a) conducts current through many deep-etched distributed Bragg reflector (DBR) grating periods. (b) Current bypasses DBRs with intra-cavity contacts.

Defense Systems and Assessments Investment Area

Advanced Optics for Military Systems
130699

Year 3 of 3
Principal Investigator: D. V. Wick

Project Purpose:
Persistent surveillance is becoming increasingly important in many national security applications. The ability to survey a wide area from long ranges for extended periods of time and correctly identify a face or object (car, weapon, etc.) quickly once it enters the field-of-view (FOV) is extremely important. However, the diametrically opposed needs to observe a wide area and maintain extremely high resolution for detection, recognition, and identification present a fundamental dilemma for any imaging system. Even with advances in focal plane array technologies, multiple systems must still be used unless a compromise in capability is acceptable (i.e., smaller FOV and/or lower resolution). Conventional systems typically use gimbals to slew the high-resolution camera.

If resolution requirements demand an entrance pupil >4ï 6 inches, reflective telescopes are required rather than refractive lenses. Unfortunately, zoom reflective systems are extremely limited (<2X); unlike lenses, mirrors cast ñshadows,ò and block light, making it extremely difficult to change the magnification of a telescope. The FOV of most reflective systems is comparable to "looking through a soda straw," and so the system must be gimbaled to cover a wider area.

Our approach will be to use variable-radius composite mirrors to change the magnification of a telescope without macroscopic motion (see D.V. Wick, et al., Proceedings SPIE 6307 for details). We were the first group to propose and demonstrate a "zoom" reflective system using variable focal length elements (US Patent # 6,977,777). However, our demonstrations were limited to small apertures (<30 mm). The envisioned applications require larger aperture active elements (>4 inch) to prove capability. Because this development requires very basic material development and finite element modeling, this project will provide the sound scientific foundation to create larger-aperture, variable-radius composite mirrors. If successful, we will have solid justification to solicit Work for Others (WFO) funding for system development.

Summary of Accomplishments:
We have successfully designed and demonstrated a push-button zoom riflescope. Using finite element modeling (FEM) along with experiments on adaptive polymer lenses, the team integrated electronic actuation and built a demonstration riflescope that toggled between 1X and 4X in less than 0.5 seconds. This is currently being integrated into a prototype riflescope for the US Army.

Next, we began to investigate thin-shelled composite mirrors for larger aperture, variable FOV systems. Composite mirrors are lightweight, replicated mirrors (thus lower cost) that can be actuated to change shape for aberration compensation. We have demonstrated that variable radius-of-curvature is possible with these mirrors, and we have demonstrated the principals of adaptive optical zoom with a reflective telescope.

Telescope systems rarely have zoom capability. Unlike similar lenses, which refract light, on-axis telescopes have obscurations and/or holes that block on-axis bundles and pass light through the center of mirrors. This makes it very difficult to design a zoom system where mirrors move longitudinally, as in a conventional zoom lens. Off-axis configurations are also very difficult due to the extremely tight tolerances. The only zoom telescopes that have been published, to the best of our knowledge, are academic demonstrations that were limited to ~4X. Under this project, we have demonstrated 10X zoom from a variable radius adaptive zoom design.

We completed and validated a FEM in ANSYS (an engineering simulation software). By testing coupons in a 4-point bend test, we ascertained Young's modulus, shear modulus, and Poison's values along each axis. We then fabricated an 8-inch diameter, 2m radius of curvature mirror and validated the FEM with point load testing. We analyzed potential actuation schemes in FEM, acquired actuators, and began to integrate those into a mounting to change the radius and maintain wavefront fidelity. This project has proven viability of variable radius mirrors.

Significance:
US strategic capabilities in persistent surveillance have atrophied, while threats to our security are increasing at an alarming pace. National leadership has recognized this situation, generating an interest in new technologies that fill existing operational gaps. Success in this project will provide the national security community — including DOE, DHS, and DoD — advanced capabilities that can be tailored to address a range of international and domestic threats. Development of the proposed system will provide the technology to field flexible, low-powered surveillance systems capable of detecting, recognizing, and identifying people/objects, and monitoring activities (at operationally relevant ranges) that pose a threat.

This project serves our national security mission by providing world-class scientific research capacity and advancing scientific knowledge. Both the adaptive polymer lens and the composite mirror work will serve both DOE and DoD personnel and infrastructure security missions. As part of this project, we demonstrated the concept of a push-button zoom riflescope. The Army is funding a transition development, and we believe this could prove extremely advantageous to the warfighter. We fully anticipate that the US Army will be demonstrating a prototype system in the near future based on this work.

Similarly, the large aperture, variable-radius composite mirrors will potentially provide a valuable tool that can be used for multiple Intelligence, Surveillance, and Reconnaissance (ISR) applications. Variable radius mirrors will provide a significant advantage for ISR applications that are restricted in size, weight, and power (SWaP). There is a great deal of interest in persistent surveillance for both air and space platforms, and a system that can vary its field-of-view in a SWaP consistent package will provide a revolutionary benefit to our national security mission.

Under this project, we started to prove the viability of this approach, and we are hopeful that we can find further funding to develop a large aperture, reflective zoom system using thin-shelled composite mirrors for high altitude and space ISR missions.

Refereed Communications:
C.C. Wilcox, M.S. Baker, D.V. Wick, R.C. Romeo, R.N. Martin, and B.F. Clark, "Measurement and Model Validation of a CFRP Deformable Mirror," to be published in *Applied Optics*.

Highly Producible Focal Plane Array
130700

Year 3 of 3
Principal Investigator: S. S. Mani

Project Purpose:
Sandia Space Programs presently relies on industry to design and fabricate high-performance focal plane arrays (HPFPAs). R&D investment in next generation FPA development is an essential springboard to establish technology and capability that is within reach of a full system development program.

This project addressed the gap between identification of performance and manufacturability improvements for existing products through designing and fabricating a readout integrated circuit (ROIC), focused on the joint design between Sandia and external vendor, Teledyne Imaging Sensors (TIS).

The HPFPA is a large format (2K x 2K pixel) mid-wavelength/short-wavelength two-color infrared (IR) FPA hybrid focal plane array with digital signal outputs designed for space applications. The HPFPA is assembled from 4-edge butted ROIC and utilizes a detector fabricated from a single piece of detector material. The project addresses the manufacturability aspects for a large two-color focal plane array by tiling four 1K x 1K pixel, non-stitched, pieces. The project focused on the joint design collaborating with TIS where TIS provided the analog portion of the design and Sandia did the digital part of the design. Sandia had the overall responsibility of the integration and performed the top-level simulation verifying and validating the design. This design has been one of the largest mixed-signal design obtained from the design team. Overall assembly concepts were addressed. The project fabricated components for the overall assembly using surrogate parts for the RIOC and detectors while performing wire bonds on the mock assembly. TIS designed the two-color detector, which was unfortunately not fabricated due to funding limitations. This effort successfully addressed the design aspects for a large two-color focal plane array. This effort extends the existing FPA design for single color to a joint two-color design between TIS and Sandia. Sandia's extensive design infrastructure was effectively leveraged.

Summary of Accomplishments:
In summary, this HPFPA project supported a joint design between Sandia and Teledyne Imaging system for a two-color focal plane array design. TIS was selected as the industry partner (contractor) for the HPFPA project. The industry partner was tasked to provide the pixel and analog design through A/D conversion for the readout integrated circuit (ROIC). Teledyne provided a design that was based heavily on the design of a previously implemented ROIC. The bias circuitry, pixel, column buffer, line driver, vertical scanner, horizontal scanner, and analog-to-digital converter designs are very similar and in some cases identical. The primary differences are in changes to physical layout to accommodate HPFPA's two-color 20-um pixel vs. the earlier design one-color 18-um pixel. Sandia received significantly more design information under the HPFPA work due to the necessity of information sharing to complete a joint ROIC design. The design information has proven extremely valuable in resolving earlier product anomalies — it has allowed Sandia to move from a trial and error mode of troubleshooting to a model- and simulation-driven anomaly resolution. In particular, bias generator schematics have helped to provide insight necessary to achieve optimum performance via register set tuning. They provided a path for resolution of several Anomaly Resolution Team activities. The final HPFPA design was fabricated in TowerJazz foundry. The project supported developments in the assembly processes for large area imaging sensors. The design experience has provided knowledge to the design team in mixed mode simulations leading to Sandia's procurement of a critical mixed-mode tool for future FPA designs.

Significance:
Advanced Space Program concepts are presently under development in the Space Mission Engineering Program Office. The user community is looking to Sandia to provide concepts for next generation systems for a variety of government agencies. The performance of many of these systems is limited by present state-of-the-art in focal plane array technology. Advances in FPA architectures, optimized for this mission area, could bring a significant increase in performance, specifically in minimum detectable signal.

Boundary-Layer Transition on Maneuvering Hypersonic Flight Vehicles
130705

Year 3 of 3
Principal Investigator: D. W. Kuntz

Project Purpose:
Boundary-layer transition (BLT) is the phenomenon that occurs within the boundary layer of flight vehicles when the flow changes from laminar to turbulent. As this process occurs, flow properties change significantly and aerodynamic heating rises drastically. Transition on ballistic flight vehicles has traditionally been predicted by correlations based on ballistic reentry vehicle (RV) flight-test experience. The class of vehicles intended to fulfill a prompt global strike (PGS) role will fly long duration trajectories, and accurately predicting boundary-layer transition would mean less conservatism in heatshield thickness. Current approaches are insufficient to address this critical need.

Numerical techniques for predicting boundary-layer transition based on stability theory are becoming the state-of-the-art for hypersonic flight. One such tool, STABL, funded by Sandia and the Air Force Office of Scientific Research (AFOSR), was developed to provide this predictive capability. The work outlined in this report combines STABL calculations with Sandia flight vehicle experience with the intention of developing a prediction capability for transition of hypersonic flight vehicles.

The objective of this effort is to develop a state-of-the-art transition prediction capability for hypersonic flight vehicles, a capability that is essential for the successful design of PGS weapon systems. The thermal protection system (TPS) of a PGS vehicle makes up a significant fraction of the mass. The uncertainty inherent in current BLT prediction techniques requires that these vehicles carry a significant margin in TPS thickness. Reducing this uncertainty through the development, application, and verification of state-of-the-art BLT prediction techniques could significantly reduce the required excess TPS material, enabling the design of a system otherwise not possible. This effort is broadly applicable to all types of hypersonic flight vehicles. An improved transition prediction capability will benefit all subsequent Sandia flight test programs as well as systems currently under development by other organizations.

Summary of Accomplishments:
The flight vehicles to be studied were determined and prioritized. Stability calculations have been completed for fifteen ballistic flight vehicles with thermal protection systems made of four different materials. The N factor, the natural log of the integrated amplification factor of the most unstable disturbance frequency, has been computed for each vehicle at the initial indication of transition. Preliminary stability calculations have been completed for a more-complex flight vehicle based on 3D flowfield solutions and for a similar flight vehicle scheduled to fly in the near future. In addition to these stability calculations, additional studies have been performed, including investigations of: 1) the effects of blowing on stability results, 2) the effect on computed N factors as transition moves forward on a ballistic vehicle, 3) N factor histories during reentry, 4) surface chemistry of specific thermal protection systems during reentry, 5) the effects of atmospheric variation on computed N factors, and 6) the effects of surface temperature variation on computed N factors.

In addition to the analyses described above, a series of technical interchange meetings (TIM) were held, at which the results of the investigations described above were presented to transition experts from academia, private industry, and government laboratories. The conclusions presented have resulted in redirected research at multiple facilities.

Significance:
The PGS mission is currently a critical national security need, and efforts to develop systems of this type are being undertaken by the DoD, with potential applications by DOE and other federal agencies. Sandia is currently serving as the Vehicle Integrator for the Army's Advanced Hypersonic Weapon (AHW) Program, a technology development effort intended to support the development of a PGS system. A thorough understanding of boundary layer transition on hypersonic flight vehicles is critical to the design of the heat shield for these systems, and the successful completion of this project provided a new level of understanding of this phenomenon for these types of vehicles.

Directed Robots for Increased Military Manpower Effectiveness
130707

Year 3 of 3
Principal Investigator: B. R. Rohrer

Project Purpose:
The purpose of the project is to increase the effectiveness of the armed forcesô unmanned vehicle operators by developing, in the unmanned vehicles, the capability of correctly interpreting high-level commands and of handling low-level environmental interactions automatically.

Existing military ground robots are almost universally teleoperated and occupy the complete attention of an operator. They may remove a soldier from harm's way, but they do not necessarily reduce manpower requirements. Current research efforts to solve the problem of autonomous operation in an unstructured, dynamic environment fall short of the desired performance. In order to increase the effectiveness of unmanned vehicle (UV) operators, we propose to develop robots that can be "directed" rather than remote-controlled. They are instructed and trained by human operators, rather than driven. The technical approach is modeled closely on psychological and neuroscientific models of human learning. Two Sandia-developed models are utilized in this effort: the Sandia Cognitive Framework (SCF), a cognitive psychology-based model of human processes; and BECCA, a psychophysical-based model of learning, motor control, and conceptualization. Together, these models span the functional space from perceptuo-motor abilities, to high-level motivational and attentional processes. We have demonstrated the control of robots in unstructured environments using scripted speech commands. In year three, we propose to demonstrate the much more challenging task of control using unscripted speech.

Summary of Accomplishments:
We demonstrated the basic principles of directed-autonomous behavior in unstructured environments. In the second year, we directed the robots using scripted speech commands. The robot was directed with specific commands "hide" and "seek." It was used to alternately search for high- and low-contrast visual scenes in a cave-like structure, relaying images wirelessly to the operator outside. In the third year, the same algorithm drove two separate hardware platforms, a Coroware CoroBot and a seven degree of freedom Barrett WAM™, in unstructured learning tasks.

New learning algorithm development:
In order to scale-up the technical approach to more-challenging environments and more-sophisticated hardware, new learning algorithms for feature creation and reinforcement learning were developed. Although there are many existing feature creation and reinforcement learning algorithms, these were found to make assumptions that were not appropriate for our team's approach.

Communication of Results:
The progress achieved in this project has been reported in a number of forums. Two videos for general audiences has been produced and published on YouTube. Eighteen conference papers and talks have been submitted and/or presented to a wide variety of technical audiences. Five of the talks were invited. A journal article has been published in the *Journal of Artificial General Intelligence* and another in the *International Journal of Computational Linguistics Research*. The focused feedback from technical experts during these exchanges has accelerated development efforts significantly.

Significance:

The goal of this project is to meet an immediate and pressing national security need, the DoD goal to "do more with less." By accelerating the transition to automated robots filling critical military roles, this work will alleviate some of the load on warfighters and position Sandia to help guide this transition. This capability is also likely to help meet DOE meet its challenge of securing critical assets and sites.

Refereed Communications:

B. Rohrer, "Concept Acquisition for Dialog Agents," *International Journal of Computational Linguistics Research*, vol. 1, pp. 189-201, 2010.

Malware Attribution through Binary Analysis
130715

Year 3 of 3
Principal Investigator: S. A. Mulder

Project Purpose:
One of the difficult problems in computer security is the lack of attribution of malicious activity. Even if malicious programs are discovered, tracing them back to an original source is often extremely difficult, if not impossible. Even correlating the activities of a single group using multiple tools can be challenging. Sandia is in a unique position, through our Footsteps Lab and other related efforts, to develop advanced capability to respond to national-level threats to our information systems. We propose to build the foundation for a long-term program in the area of collecting evidence for attribution.

Experts currently do most attribution work manually. This process is slow, relies on extensive reverse engineering capability, and is naturally error-prone. Sandia has been one of the leaders in solving these problems manually through our access to interesting data and ties to various government organizations. The focus of this research effort has been to dramatically improve the speed and accuracy of our current attribution efforts through automation and to make new discovery possible through a normalization process.

Summary of Accomplishments:
During the course of this research, we learned about the strengths and limitations of binary analysis.

- We designed and tested a scalable modular binary analysis framework called Oxide.
- We demonstrated auto-dependency resolution, third-party integration, and technology isolation in our framework to enable domain-specific developers to work in the system without knowledge outside their domain.
- We demonstrated identification of build chain using our framework.
- We demonstrated the development and application of basic actor models using our framework.
- We analyzed a huge corpus of malicious and normal software to harden our feature extraction technologies.
- We built a foundation for future research in the area of binary analysis.

Significance:
The inability to apply attribution to malicious cyber behavior is one of the limiting factors in current security models. The potential impact of this research is significant. It directly contributes to our ability to understand the threat space, providing insight into who our adversaries are and what capabilities they possess. It also provides a basis for appropriate response to malicious activity. We do not claim the research will provide definitive attribution, but instead, that it will greatly contribute to a body of evidence that supports plausible attribution. This directly addresses one of the primary gaps in national cyber defense capability.

Next Level Technology Development for Satellite-Based Processing Architectures
130720

Year 3 of 3
Principal Investigator: J. L. Kalb

Project Purpose:
Sandia is currently developing new satellite payload processing and data communication architectures that are integral to providing intelligence about worldwide threats to our nation's security. These architectures focus on increasing mission flexibility, accommodating enhanced sensor performance, and optimizing payload size, weight, and power (SWaP) consumption. The focus of this effort is to define a network-based architecture that is scalable, reliable, and reusable. Sandia has been able to make significant progress in the specific architectural areas of network communication, model based design, sensor data processing algorithms, and reconfigurable computing. In the area of network communication, much progress has been made evaluating high-speed serial protocols and potential topological configurations, developing tools to easily automate communication performance modeling, and evaluating communication performance once recovery from faults has taken place. Results from prior analysis indicate there are two major findings that affect the system communication design and performance, both prior to and after fault scenarios. These findings are that network communication and reconfigurable field programmable gate arrays (FPGAs) are critical to architecture performance and reliability. Several areas relating to these two fundamental components pose technical challenges that need to be addressed in order to effectively implement these architectures. These challenges include mitigating single event upsets (SEU) in static random access memory (SRAM)-based FPGAs, reducing the large size of FPGA configuration bit files, placing processing nodes in a distributed, network-connected architecture, and recognizing and recovering from fault conditions. The objective of this work is to investigate efficient approaches to SEU mitigation and device configuration and to design methods to optimize architecture topologies for communication performance and fault detection and recovery.

Summary of Accomplishments:
We developed mathematical models describing distributed processing architectures and traffic patterns as optimization problems. We used algorithms to approach optimal solutions not consistently achievable by manual decisions. Failure analysis on results and iterated strategy for robustness against network failures were performed. We ported open-source solver to embedded operating systems (OS) and assessed the feasibility of on-board optimization.

We analyzed interactions of space systems, assessed vulnerabilities and failure scenarios of systems and found solutions in a semi- or fully autonomous way. The ability of systems to self-monitor and protect the hardware/software assets of a payload was researched. The fusion of software and hardware approaches, using the latest fault tolerance and plug and play research, was conducted.

We developed a method to enable dynamic reconfiguration of an on-board system using a SpaceWire network. Booting an FPGA locally with a minimal bit file and partially configuring it remotely over a serial interface was performed.

We created an application of decompression at the end user instead of upstream. We offloaded the processor from the task of compression or decompression and leveraged the results from partial reconfiguration (PR) research to make this approach feasible.

Vendor support for single event effects (SEE) mitigation of electronic components up to now is primarily triple modular redundancy; this is expensive in terms of SWaP and, in many cases, not feasible. Soft-core processors are not typically used in SEU susceptible devices but provide an important level of flexibility for space processing using reconfigurable devices. We mitigated soft-core processors and verified that they are reliable. We developed a device under test (DUT) card that provides flexible single-event upset immune reconfigurable field programmable gate array (SIRF) test platform for processor, multigigabit transceiver (MGT), and digital signal processing (DSP) characterization.

We implemented an overhead persistent infrared (OPIR) target-detection algorithm in a reconfigurable and scalable on-board satellite processing architecture. We incorporated and extended several technologies that had been independently developed at Sandia and were collaboratively brought together for this demonstration. Creation of functional space-ready hardware populated with vital algorithms that are proven effective for a high-profile national security mission was completed.

Significance:
Sandia's space mission and remote sensing (SMRS) program is an integral part of DOE's nonproliferation mission, in addition to the DHS and the national security missions. To keep pace with new emerging threats, we must continually advance the capabilities of our intelligence and remote sensing systems. The availability of this architecture can address the challenges of design complexity, design reuse, bandwidth, and redundancy so that future design resources can be better spent developing capabilities to meet the needs of our collaborators.

Silicon Microphotonic Backplane for Focal Plane Array Communications
130727

Year 3 of 3
Principal Investigator: A. L. Lentine

Project Purpose:
Future large focal plane arrays (FPAs) (~10^8 detectors) will have on- and off-chip bandwidth requirements exceeding 1Tb/s. Furthermore, many focal plane arrays must operate at low temperatures in a cryostat with a few percent cooling efficiency. Hence, each watt of dissipation on the FPA causes 20-to-30W of additional cooling system dissipation. Electrical communication from a FPA, while the standard, is undesirable because of its relatively high power dissipation, increased thermal conductance caused by conductive electrical lines, and innate susceptibility to electromagnetic interference. Existing optical transceiver solutions require large, complex mechanical assemblies, have significant scaling limitations, and dissipate even more power. Here, we propose silicon microphotonic communications to enable massive on- and off-chip bandwidths (>1Tb/s) on a FPA. A silicon microphotonic backplane will be developed that will fit into the current FPA electrical backplane solution developed by the FPA LDRD project. All data will be transferred on and off chip with a single optical fiber, thereby, simultaneously minimizing thermal conductance and susceptibility to electromagnetic interference. Further, the silicon microphotonic backplane will dissipate >100X less power than electrical or competing optical solutions and the optical source will be located off-chip and outside the cryostat.

Over the past year, we have reduced our modulator power consumption to under 10fJ/bit, representing a new record in ultralow power modulators. Further, by integrating heater elements and temperature sensors directly into our modulators, we have demonstrated the ability to hold the resonant frequency of our modulators stable across a 55 °C temperature excursion, another first for silicon photonics. Further, we demonstrated both direct and hybrid integration techniques offering potential for radiation hardened and high-speed operation, respectively. Finally, we have matured fiber-attach mechanisms and germanium detector technologies. We will demonstrate cryogenic operation along with wavelength-division-multiplexed communications across four sites on a silicon photonic backplane, feats never previously demonstrated.

Summary of Accomplishments:
We have a number of key demonstrations, including: 1) world record low energy optical silicon photonics modulator (3 fJ/bit) with low voltage complementary metal oxide semiconductor (CMOS) drive, 2) integration of silicon photonics with Rad-Hard CMOS, 3) demonstration of a new class of thermal silicon micro-photonic devices, 4) demonstrated wavelength stability of a microring resonator over a 55 °C temperature range, 5) demonstration of a 120 cm silicon photonics backplane, 6) hybrid integration of a silicon photonics modulator with a 90 nm CMOS driver, 7) the first investigation of resonant wavelength variations from manufacturing process variations, 8) a thorough investigation of the loss in the waveguides in our silicon photonics platform, and 9) demonstration of a silicon photonics 4-wavelength transmitter at 10 Gb/s per wavelength. The project is responsible for two filed patent applications, two published and three additional submitted journal publications, and several conference publications.

Significance:
The results of this effort will be applicable to many DOE and DoD missions. This silicon microphotonic communications platform will be critical to the advancement of high performance (HPC) and embedded computing applications in addition to the scaling of very large, high-speed digital imagers. HPC is critical to maintaining a nuclear deterrent and very large, high-speed digital imagers are critical to minimizing the proliferation of weapons of mass destruction, two stated goals of the DOE Strategic Plan.

Refereed Communications:
W.A. Zortman, D.C. Trotter, and M.R. Watts, "Silicon Photonics Manufacturing," *Optics Express*, vol. 18, pp. 23598-23607, 2010.

M.R. Watts, "Adiabatic Microring Resonators," *Optics Letters*, vol. 35, pp. 3231-3233, 2010.

Velocity Independent Continuous Tracking Radar
130729

Year 3 of 3
Principal Investigator: D. W. Harmony

Project Purpose:
The detection and tracking of moving vehicles is an increasingly important remote surveillance problem. Radar systems (e.g., joint surveillance and target attack radar system [JSTARS]) typically excel in ground moving target indication (GMTI) because of their unparalleled wide-area search capabilities. However, existing radars are severely limited in their ability to follow individual vehicles over typical velocity changes experienced while maneuvering in traffic. All GMTI radars rely on the vehicle's motion for detection against ground clutter. When a vehicle slows or stops, tracking becomes difficult and is virtually impossible for present systems. This research investigates techniques and algorithms for tracking mobile high-value targets over realistic velocity changes based on unique radar capabilities developed at Sandia. The three-year effort will culminate in flight tests demonstrating vehicle tracking in real world scenarios.

This project is developing methods to combine historically disparate radar modes, in a new manner that allows vehicle tracking through all phases of motion. Ground surveillance radar systems typically operate in either a synthetic aperture radar (SAR) mode, imaging stationary objects, or in a wide-area GMTI mode, searching for movement. Both modes are limited by the range of vehicle speeds they can accommodate, consequently resulting in system-dependent velocity bands that neither mode can handle. Vehicle tracks are usually lost as they pass through these bands. However, by simultaneously processing a single radar data stream using both SAR and azimuth monopulse GMTI techniques, the blind velocity gaps between bands can be reduced or eliminated. In conjunction with a tracker, this enables continuous surveillance of a high-value target through stops and turns.

Summary of Accomplishments:
This project developed techniques and algorithms for tracking maneuvering ground vehicles through stops and turns with airborne radar. The primary accomplishment this year was to implement the algorithms in real-time software and conduct flight tests that successfully demonstrated vehicle tracking. This was a significant first step towards the development of a radar surveillance capability similar to optical full-motion video.

Significance:
Sandia's national security collaborators are being tasked to monitor mobile targets in the DOE's proliferation detection arena. There is an explicitly stated need for continuous tracking of a single high-value vehicle. This research is the best approach to support national security missions.

Wavelength-Division-Multiplexed (WDM) Free-Space Optical Communication Using a High Repetition Rate-Coherent Broadband Short-Pulse Laser
130731

Year 3 of 3
Principal Investigator: J. Urayama

Project Purpose:
There is a great need for secure, high-speed, operationally flexible communication systems for rapid situational awareness operations in the field. These operations demand direct and reliable communication systems for transmission of time-sensitive and high-volume data. Existing technologies based on radio frequency (RF) and conventional fiber-based networks do not meet this combination of requirements. The purpose of the project is to develop free-space optical communication (FSOC) using line-of-sight atmospheric delivery of encoded broadband laser beams that offer the bandwidth to deliver high volumes of data at gigabits-per-second rates. This capacity is enabled by executing time- and wavelength-division-multiplexing (TDM-WDM) across the coherent optical spectrum to generate many parallel channels in a single laser beam. Security is achieved through the directionality of the laser beam and also through encoding and decoding schemes using both amplitude and phase modulation technologies. Additional measures such as pulse shaping and coherent detection are employed to enhance security and enable applications for secure key distribution.

Because both the high-speed and security capabilities rely on the delivery of broadband femtosecond laser beams, challenges in the project will center on spectral phase manipulation and preservation during the encoding and in the presence of atmospheric turbulence that imparts wavelength-dependent scintillation effects. Phase manipulation will be optimized using in-house pulse shaping technologies. This interdisciplinary effort involving short-pulse lasers, pulse shaping, telecommunication methods, atmospheric propagation expertise, and signal processing poses great technical challenges. The project will be dedicated to achieving a balance of modulation rates, channel generation, and beam delivery for a high-speed, high-security FSOC link. With these combined efforts, a functional WDM FSOC link will be established to prove level of performance.

Summary of Accomplishments:
Over the life of this project, an FSOC link based on a femtosecond broadband laser was developed and tested. The transmitter was constructed, employing the TDM-WDM approach, to make full use of the broad spectrum. Commercial off-the-shelf (COTS) modulator technology was incorporated into the setup to enable both high-speed amplitude and phase modulation. Interferometric relative phase modulation was also developed via optical pulse shaping and spectral interferometry for highly secure transmission. Together, these designs allowed for three modes of modulation within the transmitter. The receiver package consisted of demultiplexing waveguide arrays and a high-speed detector for the ON-OFF keying, while a specific receiver was constructed for the phase detection that enabled fast detection of phase shift keying. For the relative phase modulation, a spectral interferometer was implemented to decode the spectral phase information across the broad spectrum. In-laboratory FSOC transmission measurements over a span of 40 meters registered proof-of-principle 1-Gbps transmission levels in the high-speed mode at practically error-free levels. Outdoor tests were conducted to test the performance of the FSOC link. In preparation for these tests, indoor verification experiments were conducted using phase plates, mainly to evaluate the collection capabilities of a propagating beam. These results showed the requirements for a simple collection optics set. High-speed amplitude and phase modulation could operate at 1 GHz, limited by the performance level of the COTS hardware. Bit error rates for the spectral channels with open eye diagrams were better than 10^{-5} without any adaptive

optics in place. Interferometric relative phase modulation demonstrated the delivery of spectral phase information over the same distances. All three modes of operation showed promise as means for femtosecond, broadband FSOC.

Significance:

The project works a critical area of national security by improving secure battlefield communications to significantly enhance data rates with minimal risk of interception. If successful, the technology developed herein is readily extendable to other tactical and strategic applications. The results of this project will directly benefit other missions in intelligence surveillance and reconnaissance (ISR) and give Sandia a competitive advantage for funding in those areas.

High Frequency RF Effects
131503

Year 3 of 3
Principal Investigator: L. D. Bacon

Project Purpose:
Satellite communications provide an important capability to military/civilian operations. Today the loss of a small number of satellites could greatly influence the global economy as well as reduce the US military's ability to exert their influence around the globe. We propose to conduct an effort composed of theoretical, numerical, and experimental work to understand the potential of high radio frequency (RF) to disrupt satellites or other electronic systems. It is our understanding that previous electronics requirements and testing may not have uncovered all of the effects that may be enabled by modern equipment. The primary goal is to understand the fundamental mechanisms of effect and their scaling. Achievement of this goal will provide the information needed to determine if an adversary could design and build a system to disrupt our critical electronic systems. Public domain literature indicates that high-powered, high-frequency (HF) RF systems that might be able to achieve previously unstudied effects may be due for implementation in less than a year.

Summary of Accomplishments:
To accomplish our objective, we produced models of the interactions, conducted simulations, and performed measurements to identify the mechanisms of effects as frequency increased. Our purpose was to answer the questions, “What are the tradeoffs between coupling, transmission losses, and device response?” and, “How high in frequency do effects continue to occur?” Using full wave electromagnetics codes (EIGER, HFSS, FEKO, and COMSOL) and a transmission-line/circuit code (LineCAP), we investigated how extremely high-frequency RF propagates on wires and printed circuit board traces. We investigated both field-to-wire coupling and direct illumination of printed circuit boards to determine the significant mechanisms for inducing currents at device terminals. We measured coupling to wires and attenuation along wires for comparison to the simulations, looking at plane-wave coupling as it launches modes onto single and multiconductor structures. We simulated the response of discrete and integrated circuit (IC) semiconductor devices to those high-frequency currents and voltages using COMSOL, SGFramework, the open-source General-purpose Semiconductor Simulator (GSS), and Sandia’s Charon circuit/semiconductor device physics codes.

Significance:
DOE, DoD, and other federal agencies rely on satellite communication systems for day-to-day and special operations. Loss of these systems would compromise the ability of the US to defend itself. These losses would compromise the US ability to extend its influence around the globe, leaving assets at risk. Determination of vulnerability will enable efforts to protect valuable electronic assets. Determining where vulnerability does not exist prevents unnecessary costly modifications.

Security through Unpredictability
131541

Year 3 of 3
Principal Investigator: M. Berg

Project Purpose:
Information system defense is currently engaged in an unfavorably asymmetric struggle with sophisticated adversaries. Standardized instruction sets, protocols, and hardware interfaces make our systems too uniform and predictable, allowing our adversaries to exploit these systems en masse using minimal reconnaissance. Today's defense systems do very little to directly address this asymmetry, relying instead on reactive technologies such as signature matching and patching. Truly effective information security measures must focus on eliminating the attacker advantage intrinsically.

This research will develop diversity technologies that eliminate certain classes of security vulnerabilities from information systems. For example, we will develop randomized instruction sets that can hinder propagation of malicious code. These technologies will be based on fundamental theories of information system security (being developed as part of this research), allowing us to scientifically determine where and how to incorporate diversity for the greatest security impact.

Summary of Accomplishments:
We designed a randomized instruction set that should be amenable to implementation in future processors. We modified both the GNU (GNU's Not Unix) assembler (commonly known as “gas”) and the as86 assembler to generate randomized instruction sets. We modified the udis86 disassembler to support randomized instruction sets. We modified the QEMU, process machine emulator, and the basic input/output system (BIOS) used by QEMU to support our randomized instruction set. The modified QEMU provides a virtual randomized instruction set processor on which to test. We made small modifications to and compiled the LILO (LInux Loader) boot-loader and the Linux kernel for our randomized instruction set. We wrote two Sandia reports: one report documenting our randomized instruction set approach and the technical challenged that we encountered, and another report on reasoning about computer security and new mitigations for vulnerabilities.

Significance:
New techniques for building secure systems will be important in helping Sandia fulfill its mission of developing high-assurance systems and in satisfying our country's cyber security needs. DHS and DoD are responsible for high-assurance information systems, as are vendors of commercial products, and could use Sandia-developed technologies to help secure their systems. This would result in more secure information systems for national security applications, management of critical infrastructures, and control of safety-critical systems. We are currently identifying applications for the randomized instruction set within Sandia's mission areas. The report on reasoning about computer security is already being applied to designing the security architecture for another project.

2D Tracking of Maneuvering and Closely Spaced Targets and Fusion into 3D Tracks
141541

Year 2 of 3
Principal Investigator: T. J. Ma

Project Purpose:
In time-critical tracking problems, multiple sensors may observe one or more moving objects. The sensor data are processed in real-time, with the goals of discriminating the separate target objects, tracking their progress in each sensor's dynamic field of view, and combining information across sensors to estimate 3D object positions as a function of time. Maneuvering targets presents a great challenge to both 2D and 3D tracking since its dynamic motion can be very different from previously estimated motion. If the maneuver behavior is not well modeled, it will cause a large error in the target's estimated position, velocity, and acceleration, and potentially the target will be lost. Using multiple filter models to estimate the target's overall dynamics is appealing, but when to switch between models is challenging. Fusion of multiple sensor, 2D detections and tracks into 3D position estimates is an additional challenge. Algorithms are needed to associate tracks of the same object in each sensor’s field of view, and to combine the associated 2D tracks into a single 3D track.

Our proposed solution is to combine multiple hypotheses tracking (MHT) with interacting multiple models (IMM) filtering. Given well-designed multiple models, the IMM techniques can adaptively estimate the state of a dynamic system. Given the complexity of combining MHT with IMM, very few authors have addressed the challenging problems that we propose to research under this project, and no satisfactory solutions have been demonstrated. This project will combine and enhance the real-time tracking performance of these algorithms in the presence of maneuvering targets. The improvements to 2D and 3D tracking capability that will result from the research will enhance the performance of current and planned future Sandia sensor systems, and will help Sandia to expand its mission in real-time processing of critical sensor data.

Summary of Accomplishments:
In the areas of 2D tracking, we have successfully developed and implemented the following dynamic models: Singer Acceleration Model, Constant Velocity Model, Coordinated Turn Model, and Jerk Model. Each dynamic model was thoroughly investigated and evaluated with real world data. We successfully implemented the IMM algorithm and observed model switching when the target dynamics changed. The new IMM tracker is capable of detecting maneuvers and has demonstrated up to a 40% reduction in position root-mean-square (RMS) error during the course of the maneuver. Our algorithms have been verified and validated with real world events and integrated into our state-of-the-art tracker framework.

In the areas of 3D tracking, the following models have been implemented and investigated: Singer Acceleration Model, Constant Axial Force, and Ballistic Model. We showed that an additional Singer Model with maneuver tuning parameter adds maneuver detection capability. Using a combination of Singer, Constant Axial Force, and Ballistic provides slightly better velocity estimates. The IMM algorithm on the 3D tracker had been tested with simulated and real data. A simulation test harness has been extended to generate realistic stressing scenarios for 3D tracker evaluation.

We also developed and implemented a 2D-to-3D tracking software architecture to allow 2D tracks to be fused in a 3D tracker. Our simulation test harness can simulate and create 2D observations that are fed to a 2D tracker that generates 2D tracks that, in turn, are sent to a 3D fusion tracker to produce 3D tracks. This sophisticated software architecture requires less assumption about false alarm rates, association of 2D tracks, and sampling frequency, since most essential pieces are added to the pipeline architecture; this significantly improves our tracking performance accuracy.

Significance:

Remote sensing plays an important role in national security missions of DOE and various other federal agencies. The research performed will benefit existing and future programs designed to provide time-critical information to a diverse user community. This project will also advance scientific knowledge by the novel combination of several advanced technologies in the general field of tracking with remote sensors.

Novel Techniques for the Geolocation of Sources Using Timing-Based Sensors
141542

Year 2 of 3
Principal Investigator: D. C. Jackson

Project Purpose:
The purpose of this project is to develop algorithms and tools to geolocate sources using time of arrival (TOA) sensors in classically under-constrained scenarios. Algorithms for determining the three-dimensional location of a receiver when in contact with four standard emitters is well documented (e.g., global navigation satellite systems such as the Navstar Global Positioning System). Alternatively, one can determine the 3D location of an emitter using four TOA receivers. In scenarios where fewer than four receivers detect a signal, a unique location and event time cannot be determined. However, in some cases, additional information encoded in TOA data can be used to geolocate sources using fewer than four receivers. Two such examples are periodic sources whose pulse repetition frequency can be measured, and multiple 2-ball detections of the same sources at different times. This approach can lead to constrained geolocation problems with only one- or two-ball detections.

We propose a focused study to investigate methods and tools for the geolocation of anthropogenic sources. This study is top-to-bottom investigation, including researching methods of solving systems of equations, comparing known sources of interest with sensor capabilities and developing software capable of operating on real data sets. Potential benefits of this study include the ability to geolocate anthropogenic sources under only one- and two-ball conditions without any required configuration changes to the constellation. This capability would provide greatly enhanced space situational awareness as well as an untapped data-gathering source.

Summary of Accomplishments:
We have identified a number of methods of acquiring additional information that can be used to contribute to a TOA geolocation solution that are not routinely utilized.

A number of these methods include processing TOA data as a time-series when the source emits multiple signals, rather than considering single events in time. Approaching data in this manner can result in constrained geolocation solutions using only one, two, or three receivers. This is possible by calculating changes in range between the source and sensors over time. Time-series analysis can also be used to generate synthetic multisensor detections using only a single sensor, empowering users to apply standard many-sensor geolocation algorithms to scenarios involving a single sensor. Further, this method permits the generation of synthetic TOA data to provide increased detection capability in low signal-to-noise and sparse sensor constellation scenarios.

We have written algorithms that can be applied to multiwavelength TOA sensors capable of measuring propagation medium characteristics. These characteristics can be compared against ancillary global data measuring the same value to provide refined geolocation estimates.

We have also constructed tools that compute visible regions of space from the sensor perspective that can be used independently or coupled with other techniques to generate geolocation estimates.

Of critical importance is coupling the aforementioned processing methods with measurements from one, two, or three TOA sensors that together can enable the determination of a unique geographic location.

Significance:
The algorithms and tools we have created will provide users of timing-based sensors in civil and defense communities with the ability to geolocate sources using fewer than four sensors. The end products of this project will provide users with a significantly enhanced geolocation capability with no required changes to existing receiver constellations. This capability is important to military operations.

Air Delivered SIGINT Sensor System Study
141543

Year 2 of 2
Principal Investigator: M. R. Gramann

Project Purpose:
The detection and exploitation of electronic communications signals can be of significant tactical value in several mission areas. However, many systems designed for this purpose are relatively large and power hungry. Development of systems for signal detection and exploitation that have significantly reduced size, weight, and power would open possibility for many additional application areas and deployment concepts. The key R&D focus of this project was on development of concepts and prototype hardware for small size, low power, and wideband radio frequency (RF) signal detection. One major component of this research demonstrated the application of cutting edge Sandia S&T developed components in order to meet these design goals. The process of integrating this S&T technology for the desired application also helped us understand the limitations and constraints of the technology that can be further explored to expand the applicability to this and other problems.

Summary of Accomplishments:
One of the biggest challenges of the proposed application is the ability to perform signal detection from a small battery-powered system. To address this concern, we identified several options for a low-power solution for detection of signals over a wide frequency range. We built a prototype demonstration system to allow evaluation of these concepts. Using this prototype system, we successfully demonstrated the application of new technologies developed by Sandia to the signal detection problem. Measurements of this prototype system demonstrated the feasibility of a low-power wideband detection system. We also identified the major risk areas that would require further research for a fieldable low-power and high-bandwidth system. This allowed us to provide feedback on design requirements to the S&T team developing new component technology. Based on this design experience and results of characterization of our prototype system, we identified a specific path forward for system miniaturization and capability scaling.

Significance:
This R&D effort has generated several measurable benefits to Sandia's S&T community and national security mission areas. Through integration and application of a low technology readiness level (TRL) S&T technology, key requirements and direction was provided to influence future research. Meanwhile, the lessons learned and the developed prototype systems are already being leveraged to solve existing national security problems.

Augmented Cognition Tool for Rapid Military Decision-Making
141587

Year 2 of 2
Principal Investigator: M. L. Bernard

Project Purpose:
The purpose of this project was to create a next-generation, multimodal association system for more rapid defense assessment. According to the Rumsfeld Commission, 25 nations have or are acquiring weapons of mass destruction (WMD). Several of these have or are acquiring long-range missiles. The prompt global strike (PGS) program is seeking to counter these threats by permitting deployment of military assets within hours. Thus, PGS decisions on whether to act or not must be made with all available data and within a very short time window. Systems that mimic neurocognitive processes regarding how humans automatically uncover and link disparate information to detect co-occurrences and associations would make it possible to incorporate and process relevant decision-information faster and more accurately. Accordingly, this project worked to leverage capabilities to produce an augmenting capability that filtered through a corpus of data to uncover relevant associations in order to auto-associate episodic (what, where) and semantic (meaning) concepts permitting potentially more efficient and accurate processing of information. The human analysts' ability to extract evidence and test hypotheses across large data sets would be augmented through interface with an engineered system. This capability was intended to directly support PGS needs by creating a system that will extract evidence from multiple information sources to piece together conceptual elements identified from the input information to improve analysts' efficiency, awareness, and knowledge discovery.

Summary of Accomplishments:
For this project, we utilized and expanded upon several Sandia capabilities to model relevant areas of the brain. The focus was to develop a system that can associate multimodal information for long-term storage for the purpose of creating a more effective, and more automated, association mechanism for the military community. Using the biology and functionality of the hippocampus as an analogy or inspiration, we have developed an artificial neural network architecture to associate k-tuples (paired associates) of multimodal input records. The architecture is composed of coupled unimodal self-organizing neural modules that learn generalizations of unimodal components of the input record. Cross modal associations, stored as a higher-order tensor, are learned incrementally as these generalizations form. Graph algorithms are then applied to the tensor to extract multimodal association networks formed during learning. Doing so yields a novel approach to data mining for knowledge discovery. This report describes the neurobiology, architecture, and operational characteristics, and also provides a simple intelligence-based example to illustrate the model's functionality. These information streams could represent the multiple information types available in today's military environment. This system leverages engineered systems storage and throughput capacity along with cutting edge computational cognitive processing to enable a system that targets the rapid military decision mission needs to significantly augment the assessment and decision-making process of a military analyst.

Significance:
This capability produced a prototype capability that, with additional funding, will directly benefit military technologies and systems capabilities with the DoD, as well as benefit nonproliferation and assessment of nuclear weapons within the DOE. This project advances key elements in the ability to augment human decision-makers in the task of filtering and incorporating large amounts of data to generate associations between people, events, and/or organizations.

The significance of the current effort is that we projected a multimodal association engine that can: 1) filter through a large corpus of data to uncover relevant associations for more efficient and accurate processing of intelligence information, 2) associate links between individuals, locations, and events from various types of situation reports, and 3) use neuromorphic technology that auto-associations information from text, image, spatial modalities.

This work directly ties into the first S&T priority for DoD FY 2013-2017 planning (to reduce the cycle time and manpower requirements for analysis and use of large data sets) and into the seventh priority (to enhance human-machine interfaces to increase productivity and effectiveness across a broad range of missions).

Refereed Communications:

C.M. Vineyard, M.L. Bernard, S.E. Taylor, T.P. Caudell, P. Watson, S.J. Verzi, N.J. Cohen, and H. Eichenbaum, “A Neurologically Plausible Artificial Neural Network Computational Architecture of Episodic Memory and Recall,” First International Conference on Biologically Inspired Cognitive Architectures, Arlington, VA, 2010.

C.M. Vineyard, M.L. Bernard, S.E. Taylor, T.P. Caudell, P. Watson S. Verzi, N.J. Cohen, and H. Eichenbaum, “A Neurologically Plausible Artificial Neural Network Computational Architecture of Episodic Memory and Recall,” *Biologically Inspired Cognitive Architectures,* A.V. Samsonovich, K.R. Johannsdottir, A. Chella, and B. Goertzel, eds., Amsterdam, Netherlands: IOS Press, pp. 175-180, 2011

Leveraging Information between Heterogeneous Modeling and Simulation Tools
141588

Year 2 of 2
Principal Investigator: N. E. Miner

Project Purpose:
This research enhances modeling and simulation (M&S) capabilities for system of systems (SoS) performance assessments inherent in DoD, DHS, and DOE programs like counter terrorism, missile defense, and other national security systems. The S&T problem addressed is developing methods and an architecture that enables diverse M&S tools to use each other's information so that operational performance at SoS levels can be assessed. Although many diverse M&S tools exist today, they function at application-specific levels of scale and scope. Developing methods for effectively utilizing the results between heterogeneous M&S tools is a technically challenging problem. Previous attempts have proposed executing diverse M&S tools at the same time. These approaches are often not feasible when high-fidelity tools produce detailed information that the larger-scope, lower-fidelity tools cannot use. This research focuses on linking stochastic-based probabilistic M&S tools that cannot be described by partial differential equations. There is significant risk to developing general methodologies for leveraging information between today's diverse M&S tools. Some of this risk is mitigated by scoping the problem to explore two M&S tool pairings in particular: communications to SoS and force-on-force (FoF) to SoS. Our cutting-edge approach applies methods from multidisciplinary design optimization (MDO) and proposes a surrogate model that aggregates high-fidelity information from one tool into a computationally efficient representation that can be accessed by a larger-scope M&S tool. One high-risk element is the information aggregation verification, because information fidelity is lost during the aggregation process to provide efficient access to large amounts of information. The project is a low technology readiness level of 1-3 (basic research to prove feasibility). The research results have a high potential to impact the quantitative analyses that are conducted in support of defense and corporate decision makers because the methods will enable analyses to leverage results and information between diverse M&S tools.

Summary of Accomplishments:
This research has resulted in the development of a unique, cross-scale M&S linkage and analysis capability not otherwise available today. Research accomplishments include: 1) developed an information linkage approach and surrogate-based architecture, 2) developed multistep M&S problem decomposition process, 3) implemented and tested several surrogate models and designs, and 4) completed two proof-of-concept linkages (including design, testing and refinement): FoF-to-SoS and comms-to-SoS. The approach uses intermediate surrogate models to bridge the information gap between the M&S tools. There are numerous advantages to this approach. The M&S tools are decoupled, executing independently of each other. This enables statistical characterization of the high-fidelity performance information. The execution of the low-fidelity SoS tool is not delayed by long-duration, potentially numerous high-fidelity M&S tool iterations. The surrogate models provide dynamic access to the high-fidelity performance characterizations as the low-fidelity, SoS state changes. Linking models increases the SoS results fidelity by incorporating high fidelity, statistical performance information based on current SoS state. The approach provides a useful alternative to expensive, brute-force, high-fidelity simulations that would be computationally intractable to execute in parallel. This approach has been demonstrated through the development of two M&S tool linkages and appears to be applicable to a wide range of other M&S tools, especially to those that are stochastic discrete event simulation-based. The architecture allows for linkage between many M&S tools simultaneously with the only limitation being compute power. The architecture does not preclude other linkage mechanisms

being used in parallel, such as direct information transfer via co-simulations or high-level architecture (HLA). In addition, this research is being assessed for use within several externally funded Sandia projects, and transition partners are being actively pursued within the DoD, OSD and DOE.

Significance:

Consistent with the DOE national security mission, this research addresses SoS M&S for evaluation of integrated systems inherent to DOE, DoD and DHS missions such as physical security, Army's current force transformation, missile defense, and other national security operations. This work addresses challenges of improved global awareness and strategic information operations, as well as DoD transformation to net-centric operations. Development of these capabilities will enable Sandia to maintain a leading edge SoS assessment capability and will bring a new level of SoS analytic capability to DoD decision-makers.

Development of 3D Tools for Threat Signatures
141589

Year 2 of 2
Principal Investigator: J. L. Powell

Project Purpose:
Improved sensors are needed to detect radioactive threat sources such as nuclear weapons (NW) and radiological dispersal devices (RDD), as well as radioisotopes used in nuclear medicine and other industries. The dominant software tools used to predict the instrument response of a detector uses the gamma flux computed by a 1D radiation transport code that assumes spherical symmetry. The detector response is computed using this flux and parametric models derived from measured spectra of radioactive calibration sources. This approach works well in many scenarios, particularly when the source-to-detector geometry is well known, such as in a portal-type detection system. However, the approach can be insufficient for detection scenarios involving small sensors (a few cubic inches) and operating scenarios where the radioactive source can no longer be modeled as a point source, making it difficult to properly relate the 1D simulation to the real 3D world.

We theorize that the use of 3D, physics-based end-to-end simulations can overcome these limitations and enable the development of improved detectors. In this project, we used Sandia's high performance computing resources in conjunction with computer-aided design (CAD) tools and high-fidelity radiation transport codes to develop a capability that addresses scenarios of interest. The focus of the project is the ambitious task of developing a physics-based 3D detector response function, given that it is the key to designing optimal radiation detection systems. We developed and validated a detector response model using experimental data. Subsequently, we will compare the 3D results to those from the 1D calculation and discuss the observed performance improvements.

Summary of Accomplishments:
We designed the process for developing input into the 3D instrument response function to consist of three fundamental steps: 1) define the operating scenario using CAD, 2) perform high-fidelity radiation transport simulations, and 3) generate gamma radiation flux map. We developed the algorithm for the detector response function that computes the actual gamma ray detector response to the incident flux, and began writing code to implement this algorithm. We verified that the radiation transport calculation alone does not accurately model material-specific properties of scintillation crystals, such as energy-dependent scintillation efficiency or surface effects. We began analyzing the best approach to account for these effects. We developed a scattering template methodology to add scattering from environmental factors not included in original 3D transport simulation. We began working with the GEANT4 code to simulate scintillation within a scintillating crystal and generated initial detector response functions for simple scenarios. The GEANT4 code has different physics capabilities than the Monte Carlo N-Particle Transport Code (MCNP) that should address the inaccuracies inherent in the MCNP simulations.

Significance:
This capability will enable Sandia to respond rapidly to requests to design radiation detection systems that address a wide variety of national security missions. The ability to model complex transport environments will enable detection systems to be designed and optimized for a particular application. It will also increase the confidence of detection and improve the interpretation of results collected in the field.

This project develops a unique toolkit to enable design and analysis of complex 3D radiation detection scenarios. This capability is fundamental for further development of tools that enable the direct analysis of the response of radiation detection systems in a specific operational environment and to specific threats. The development of this toolkit will also allow Sandia to perform quality assessments of analysis software currently in use and create more robust methods for Sandia's applications.

High-Efficiency High-Power Laser for Directed Energy Application
141593

Year 2 of 2
Principal Investigator: K. L. Schroder

Project Purpose:
Laser directed energy (LDE) offers promise as a game changer in military operations with its long-cited advantages of speed of light response and precision effects. The Defense Science Board 2007 report states that, despite advances made in laser technology, size, weight, and power, logistics issues continue to limit their adoption for battlefield use. The future focus should be on laser technologies with the promise of providing smaller, lighter, more efficient systems with deep magazines enabling transportable tactical applications on aircraft, ground vehicles, and ships. Development of all-electric, solid-state laser systems is being pursued to address these requirements. Fiber laser technology, in particular, offers advantages over other solid-state lasers, with higher beam quality, higher efficiency, and enhanced ruggedness; however, scaling of fiber lasers to the required power levels will require combining of multiple emitters. Spectral beam combining (SBC) offers the diffraction limited beam quality required for long-range engagement without the complexity of precisely controlling the phase of a large number of emitters required for coherent combining. SBC combines multiple individual laser beams of different wavelengths into a single spatially coherent multicolor beam, typically using a diffraction grating. The number of beams that can practically be spectrally combined is limited and could be dramatically increased if a multicolor spectrally combined beam could be spectrally compressed to allow it to be further combined in a second stage of SBC.

We propose to develop a novel spectral beam combining and compression (SBCC) laser architecture that allows scaling to tactical LDE power levels with high efficiency, diffraction limited beam quality, and improved ruggedness in an inherently modular and scalable architecture. Successful demonstration of this architecture, which marries state-of-the art SBC with Raman fiber lasers, can revolutionize capabilities of all-electric, solid-state laser systems but requires development of Raman fiber laser technology to power and brightness levels beyond the current state-of-the art.

Summary of Accomplishments:
We developed a rigorous stochastic model, incorporating comprehensive nonlinear processes, for incoherent light and its spectral broadening in fiber. A comparison of the model and results from a carefully conducted Raman fiber experiments shows excellent agreement. We derived an analytical expression of the ensemble-averaged spectral power density that clearly reveals the physics. The model can be used to optimize the Raman fiber laser for spectral compression.

Using our model, we discovered the effect of dispersion in mitigating spectral broadening of incoherent light in optical fiber. The discovery gives us an approach to maintaining the spectral linewidth of a fiber Raman laser cavity output sufficiently narrow to be used in spectral beam combining.

Working with University of Bath we made significant progress in developing highly dispersive fiber for use in our fiber Raman laser cavity. Two approaches were pursued to realize a suitable highly dispersive fiber, and, while the resulting fibers that were drawn either had high dispersion in the wrong spectral region or had too high of attenuation to be used in our Raman compression experiments, we have learned lessons that can be applied in our future efforts to develop highly dispersive fiber for our application.

We developed a COMSOL/MatLab model to solve for the eigenmodes and dispersion in photonic crystal fiber structures for use in guiding the development of highly dispersive fiber.

We conducted Raman compression experiments, first at up to 10W and later at up to 80W, of absorbed pump power. These experiments achieved excellent agreement with our models.

Significance:
This approach is aligned to DoD mission needs in the Navy Air Warfare Center Weapons Division (NAWCWD), the Laser Weapon System in Naval Sea Systems Command (NAVSEA), the Defense Advanced Research Projects Agency Architecture for Diode High Energy Laser System Program, and the Directed Energy Shield concept for all-electric lasers for aircraft self-defense and base protection for Air Force Air Combat Command and Air Armament Center. It may be attractive for counter rocket, artillery, and mortar applications for the High Energy Laser Technology Demonstrator for Army Space and Missile Defense Command. This approach is important in that it breaks the current paradigm involving spectral beam combination and will enable, for the first time, spectral combination of very broad linewidth lasers. This will significantly reduce the complexity of a spectral beam combined high power fiber laser system since fewer amplifier legs will be needed.

The accomplishments made in this project have furthered development of the spectral compression and spectral beam combining approach and have enabled Sandia to develop partnerships with Air Force Research Laboratory (AFRL). In addition, the comprehensive model of non-linear processes acting in optical fiber is broadly applicable to Raman fiber lasers, active fiber lasers, and other applications in which understanding of non-linear wave mixing in optical fiber is important.

Refereed Communications:
D.B.S. Soh and J.P. Koplow, “Analysis of Spectral Broadening of Incoherent Light in Optical Fibers with Nonzero Dispersion,” *Optical Engineering*, vol. 50, p. 111602, September 2011.

D.B.S. Soh, J.P. Koplow, S.W. Moore, K.L. Schroder, and W.L. Hsu, "The Effect of Dispersion on Spectral Broadening of Incoherent Continuous-Wave Light in Optical Fibers,” *Optics Express*, vol. 18, pp. 22393-22405, October 2011.

High-Performance, High-Density Interconnect Technologies for Next-Generation Satellite Systems
141594

Year 2 of 2
Principal Investigator: S. E. Garrett

Project Purpose:
We propose to develop and qualify high-density interconnect (HDI) technologies currently used in commercial graphics processing applications for next-generation, high-consequence space applications. A recent advanced program that utilized complex printed circuit board (PCB) designs but standard PCB fabrication technologies experienced very low yields with high costs and lengthy delivery times. Current designs for data processing satellite applications utilize commercial, advanced field programmable gate array (FPGA) components with 1mm pitch and 1752 input/output (I/O). These commercial components require PCB designs that continue to challenge design guidelines for both the PCB layout and standard PCB fabrication technologies. Future advanced components will certainly have even higher I/O counts and finer device pitches. Our standard space-approved PCB technologies will not be able to support commercial components with pitches less than 1mm. High-end commercial products have already begun a transition to newer HDI technologies.

As components and technologies continue to evolve, Sandia must be prepared to adapt HDI technologies, compatible materials, and on-shore vendors to meet requirements for next-generation space applications. New technologies and materials must support program objectives of reducing size, weight, and power while improving high-speed, high-frequency performance. Aspects that will be addressed in this project are: 1) fabrication process capability, 2) materials compatibility, 3) thermal management and power dissipation, and 4) improved reliability of high-density interconnect circuit features.

In order to support the next-generation space applications, we must initiate a project now to develop and qualify HDI technologies that will be compatible with future commercial components. The objective of this project is to deliver high-complexity, high-mix and low-volume products for space applications that are anticipated in two years. The proposed technologies will produce electronic modules with improved reliability, shorter delivery times, and lower costs. To adequately support future export-controlled information programs, it is important to develop a robust technology capable of being fabricated at multiple vendors.

Summary of Accomplishments:
We gained our initial exposure to HDI computer aided design issues by translating two conventional printed circuit board designs to HDI technology designs. Two lessons learned were: 1) development of internal computer-aided design (CAD) capability for HDI technology is highly recommended and 2) in order to use HDI technology efficiently, the decision to use HDI technology and HDI tools must be made at the schematic level rather than later in the process. Sandia also gained experience in evaluating new materials that are compatible with HDI processing temperatures and meet the requirement of the Reduction of Hazardous Substances directives.

We gained extensive HDI fabrication experience by fabricating three test panels and two functional designs. Collaborations with commercial vendors were beneficial in understanding processing issues involved with HDI technology. The test panels enabled Sandia to evaluate critical HDI technologies such as, via reliability, fine-width conductor and space imaging, layer-to-layer registration, and laminate integrity. The principle of the test panels is to utilize coupons with incrementally more complex features. This evaluation enabled Sandia to learn the limitations of HDI technology and to establish vendor process capability. Fine-width conductor and space imaging still poses a challenge to US vendors. However, current technology is capable for next-generation components and applications. From the data generated, an initial HDI design guideline was generated. This guideline incorporated design for manufacturability issues that will enable robust designs and prevent costly delays from low production yields. The functional designs are useful for taking an electronic design through layout, fabrication, assembly and environmental testing. Successful completion of these steps is an ideal method to demonstrate a particular technology readiness level. Additional work is under way to assess the HDI technology from design through fabrication, assembly, and environmental testing

Significance:

One critical enabler of advanced electronic systems is high-bandwidth electronics. As design complexity increases, we must look beyond standard PCB technology to find suitable alternatives for the future. Future high-bandwidth electronics will require circuit miniaturization beyond the capabilities of standard PCB technology. This project will position Sandia to support applications requiring complex high-speed data processing from space. High-reliability HDI technology developed by this project will potentially support a variety of missions such as: 1) DOE nuclear weapons nonproliferation, 2) DHS programs that detect or prevent radiological, biological or chemical attacks against the US, and 3) DOE efforts to detect global warming trends from space.

This project supports our nation's satellite space missions by developing robust technologies that deliver high performance and reliability. Use of HDI technology will enable substantial reduction in size, weight, and power of space assemblies resulting in significant improvements in quality, performance, cost, and schedule. These project objectives enable extensive use of high-performance commercial components, maximum exploitation of commercial suppliers, and highly adaptable and scalable designs for multiple payloads.

To date, results of the project indicate that HDI technology is very promising for future next-generation space applications at Sandia. Assuming successful electrical and environmental testing, the team recommends HDI as a viable option for future satellite applications or other Sandia applications that utilize high I/O ball grid array (BGA) or column grid array (CGA) components. As component miniaturization continues, it will be necessary to continue to work with US vendors to ensure the fine trace and space capability is improved.

Hybrid Femtosecond/Nanosecond Pulsed Laser Machining
141595

Year 2 of 3
Principal Investigator: B. H. Jared

Project Purpose:
There is an existing demand at Sandia for versatile micromachining techniques that precisely and rapidly section composites of different known and unknown stoichiometry. Such materials, which may include metals, dielectrics, semiconductors, and organics in the same volume, are not adequately addressed with conventional methods due to a distinct lack of material selectivity or other limitations. While laser-based micromachining methods involving a single pulse duration have been pursued as a viable alternative to mechanical and chemical sectioning, no single laser source provides the combination of rapid processing, material selectivity, and material versatility required for successful processing of all composites. To address these issues, we propose researching and developing a hybrid pulsed laser technique with in situ chemical characterization, for high-throughput, feedback-controlled processing.

Summary of Accomplishments:
Work across multiple project milestones has been achieved. The integration of optical and electrical hardware has enabled the demonstration of spatially overlapped fs and ns laser pulses and of temporal controlled laser-induced breakdown spectroscopy (LIBS) triggering. Near term work is expected to complete temporal control of both laser pulses and LIBS acquisition before the end of the quarter. Machining rates have been quantified for materials of interest using the fs and ns lasers individually and combined spatially. A database of LIBS spectra necessary for closed-loop processing has been compiled for a range of materials, and signal sensitivity has been investigated across a range of laser operating parameters. Process depth has been identified as a significant barrier to effective LIBS signal collection, prompting work to implement co-linear beam delivery and LIBS signal acquisition.

Significance:
Sandia is a leader in developing advanced materials engineering and analysis techniques that provide leading-edge capabilities in microelectronics, microelectromechanical systems (MEMS), photovoltaics, etc., for DOE, NNSA, and other national security needs. The development of hybrid laser sectioning methods that address a large variety of materials, including composites, will enhance our ability to address future needs, as well as advance the mission of scientific discovery and innovation.

Laser Characterization and Prediction for Silicon Sensors
141597

Year 2 of 3
Principal Investigator: S. S. Mani

Project Purpose:
Laser illumination poses a threat to electro-optic sensors in space. Literature has addressed the predictability of laser damage as a singular thermal problem for the design of electro-optic devices. The coupled nature of thermal and electronic behavior is complex. This has not been addressed to any functional degree with respect to the quantification of damage thresholds in sensor design and fabrication. This ambitious problem involves multiple disciplines requiring parallel efforts in thermal, optical, electrical, and material sciences. In response to these challenges, we propose to identify, understand, and specify the time scales in which these coupled physical processes act through the development of predictive models simulating laser damage phenomena.

The project successfully damaged photodiodes using nanosecond pulsed lasers at 1064 nm. Preliminary predictive models incorporating basic physics indicate a reasonable match between the experimental results and the models. For the Si photodiode, three distinct damage thresholds were observed. Surface damage could precede electrical damage. The dark current measured was modeled as generation-recombination currents inducing from defects in the lattice as a result of thermal stresses arising due to heating. The defects serve as recombination centers that result in an extra flow of current into the damaged region, similar to the effect observed in metal-oxide-semiconductor field-effect transistors (MOSFETs) due to radiation damage. The model development is in progress and preliminary calculations indicate a good match between the predictions and the experiments.

The information gained through the nanosecond pulse efforts serves as the intellectual foothold needed to extend our work to the physics involved in shorter pulses (<500 ps). Having the prominent physical mechanisms of damaged identified, mitigation strategies incorporating our newly developed “Laser Hardened By Design/Process” rules will be demonstrated. In total, this effort will realize both an evaluation (testing) and modeling capability needed to assess vulnerabilities in scanning as well as staring silicon-based sensors for space applications.

Summary of Accomplishments:
The project successfully damaged photodiodes using nanosecond pulsed lasers at 1064nm. Preliminary predictive models incorporating basic physics indicate a reasonable match between the experimental results and the models.

A laser damage setup was designed and built to measure both electrical and morphological damage of photodiodes. The setup uses passively Q-switched microlaser with a modular design allowing optimization for pulse energy or repetition rate depending on experimental needs. The single pulse output of the laser was 4.9 ns (10^{-2}) duration and focused to a spot size of 16 μm (10^{-2}) for 1064 nm. LabVIEW was used to remotely control the partial beam splitter to achieve the desired energy. An electrical fixture anchored the photodiode during exposure and provided connection to the interface with equipment for electrical characterization. Dark currents were measured before and after illumination using customized LabVIEW program. Dark current was found to be a strong indicator of device performance changing over a wide range. Further, surface morphology was also monitored using a charge-coupled device (CCD) camera.

For the Si photodiode (P/N S2386-18K), three distinct damage thresholds corresponding to different levels of degradation were observed. These damages were for single-shot electrical damage, single-shot morphological damage without electrical damage, and multi-shot electrical and morphological damage. Surface damage could precede electrical damage but morphological damage did not necessarily correlate to electrical damage. The dark current measured was modeled as generation-recombination currents inducing from defects in the lattice as a result of thermal stresses arising due to heating. The defects serve as recombination centers that result in an extra flow of current into the damaged region similar to the effect observed in MOSFET's due to radiation damage. The model development is in progress and preliminary calculations indicate a good match between the predictions and the experiments.

Significance:
Sandia's mission aims to provide solutions to protect the delivery of space-enabled services and provide the capability to operate though hostile environments. The technology developed under this project will harden future optoelectronic US space systems against laser threat. This effort would enable critical decisions for missions by predicting sensor performance under hostile environments.

"ExtremeSS" Low Probability of Detection, Ultra-Wideband Communications 141602

Year 2 of 2
Principal Investigator: C. L. Gibson

Project Purpose:
Ultra-wide band (UWB) signal transmission has been lauded for being multipath tolerant and, if combined with high processing gain, of being low probability of detection (LPD). Commercial UWB views wireless universal serial bus/high-detection multimedia interface (USB/HDMI) as its "killer application," hence, they focus on high data rate with little processing gain, instead of being LPD. Federal Communications Commission (FCC) regulations and multi-hundred megabit data rates limit range to several meters —perfect for the living room.

Today's soldier fights in close proximity to the enemy, in and among buildings. This makes UWB technology attractive both for being more robust to multipath fading and LPD. However, commercial UWB is typically short range and not particularly LPD. Synchronization, UWB's Achilles-heel, is addressed using novel techniques. The existing low data rate UWB systems are not nearly as LPD or as low power as the proposed solution. The proposed technique is scalable depending if range, bit rate, or LPD is more important.

Summary of Accomplishments:
One of the greatest accomplishments is the creation of UWB system that conceals transmissions both in the time and frequency domain.

To achieve the measured performance of the overall system, several technological innovations were accomplished. First, a cascaded mixing method was used to attenuate the carrier by about 74 dB. We also designed and tested a low dispersion UWB antenna that is sufficiently compact for the warfighter communications application, outperforming commercially available UWB antennas. We also successfully implemented a Walsh transform for determining the amount of delay in a transmitted message, as well as a tracking loop to account for system drift and physical movement. Finally, we have shown that, with the aid of a chip scale atomic clock (CSAC), a system such as this can operate in a global positioning system (GPS)-denied environment.

Significance:
While this research has focused on military and special operations forces (SOF), numerous applications have been discussed with other government agencies. If data rate requirements are relaxed, the detection range can be decreased further, or the communication range can be extended. Though voice-class data rates are targeted, many other applications can be enabled by trading stealth and data rate requirements. Similarly, this system can be utilized for range detection.

Formal Methods for Latent Vulnerability Detection in Source Code
141603

Year 2 of 2
Principal Investigator: D. Bueno

Project Purpose:
Current approaches for detecting latent vulnerabilities in source code require time-intensive manual supervision and suffer from many false negatives. Popular approaches, such as fuzzing, require careful tuning to achieve good results. An ideal tool would automatically check for classes of vulnerabilities given target source code. For each vulnerability found, it would generate inputs triggering the vulnerability.

We propose to investigate the feasibility of building a vulnerability discovery tool using formal methods. Specifically, we are investigating satisfiability-based (SAT-based) symbolic execution engines. A SAT-based symbolic executor is essentially an interpreter for a program that "executes" machine instructions by representing their operations as logical constraints. Whenever one wants to know about the possible values of variables given the instructions along the current path, one simply asks the SAT solver to solve a logic problem. For example, if the current instruction dereferences a pointer, it is susceptible to dereferencing the null pointer, which will crash the program. At this point, the symbolic executor sets up a SAT problem, describing the program up to the current instruction, and asks if there is a program input that causes that pointer variable to equal "0." If so, the SAT solver can generate such an input that causes the program to dereference null.

Symbolic execution technology is at the forefront of formal methods-based program analysis. Such engines are creating a niche in program analysis because they perform very precise analysis. Another advantage of SAT-based methods is that, as just described, for any vulnerability found one can always obtain a counterexample (i.e., inputs that trigger the vulnerability).

Summary of Accomplishments:
We wrote a symbolic executor that is not specific to any instruction set architecture. It is, thus, a general platform for symbolic execution analysis. It can also be used as a convenient alternative to conjunctive normal form for encoding Satisfiability (SAT) instances. We have used both capabilities and demonstrated its efficiency.

We wrote a SAT solver that allows us to explore solver-specific heuristics when dealing with search problems.

We have discovered several software verification-specific heuristics that increase the efficiency of symbolic execution on commodity software.

Significance:
This work is highlyrelevant to DOE's scientific discovery and innovation mission. We are investigating how to use cutting-edge techniques that can potentially greatly improve best practices.

Optimization of Time-Critical Constellation Scheduling
141604

Year 2 of 2
Principal Investigator: T. P. Fielder

Project Purpose:
Evolving threats and growth in complexity of heterogeneous space-based sensing systems prove too difficult for humans to efficiently and effectively manage. Optimizing collection coverage for automated time-critical response to developing situations requires sophisticated constellation resource allocation and scheduling algorithms. Greedy solutions or other naïve heuristics often do not provide good results for all cases because they do not handle challenging problem instances. The goal of this project is to develop algorithms that optimize coverage of a set of targets using limited sensors in a real-time setting in the face of multiple dynamically varying cost functions, such as situations in which a target's position and velocity uncertainty grows over time.

Previous research, such as the traditional traveling salesman problem, attempts to reach a specified number of targets in as little time as possible by creating a graph throughout the system and visiting each target once. Another classic problem in graph theory is the vehicular routing problem in which some number of customers is visited by some smaller number of vehicles in as efficient a way as possible. Our problem is unique in that both the sensor and the target are moving; each target has a different weight, or importance, associated with it; the benefit of a target is dependent upon the view angle, or relative location, of the sensor, and the weight of a particular target continues to grow over time, indicating that it will need to be visited multiple times throughout the course of the simulation.

We evaluated: 1) scheduling algorithm performance against simulated time-critical scenarios, 2) sensitivity to update frequency of time varying costs, 3) significant challenges and tradeoffs, and 4) the benefits of the developed algorithms to a range of real-time and pre-planned missions. This work will reduce the latency over human scheduling, and we expect to significantly reduce the number of missed targets and target location uncertainties as compared to existing techniques.

Summary of Accomplishments:
We have examined a variety of novel algorithms aimed at solving the above problems. Each of these algorithms has their own strengths and weaknesses, but a few trends did appear.

In particular, it was observed that the performance of the various algorithms appeared inconsistent, sometimes performing well and other times performing poorly. This led to the realization that the distribution of the error within the system may have some impact on algorithm performance. Certain cost functions are more successful at limiting outliers while other cost functions are more successful at reducing overall system error. An Adaptive Scheduler algorithm was developed that could examine the distribution of targets within the system and determine which cost function should be used for the given scenario and modify it dynamically during execution. Many cost functions attempted to make decisions by either maximizing error reduction or minimizing travel time, but it appears that neither of these resulted in consistent performance. Rather, it is the ratio between these two that needs to be optimized.

It was also observed that there is a tradeoff between the Look Angle of two sensors collecting a single target versus collecting on separate targets. This tradeoff varied depending on the density of targets and the constellation characteristics, but was generally optimized near 45-degree scissor angle between sensors.

We also developed a threshold scheduler based on the idea that certain observables that have not been observed in many iterations tend to have high error covariance determinants and will, therefore, be very difficult to find. The likelihood of making a successful collection becomes increasingly small and we will continue to spend time ineffectively attempting to locate the target. This time is more efficiently spent collecting on targets with smaller error covariances.

Significance:
Sandia and DOE are established leaders in the remote sensing community, responsible for the design, maintenance, and operation of numerous critical assets. Challenging issues facing the national security community include the need for improved capabilities for global and theater situational awareness. This study can provide Sandia with constellation scheduling algorithms and simulation capabilities for time-critical response to developing situations for use in existing and future systems, enabling Sandia to maintain its status as a recognized leader in system technical capabilities and mission utility. This study also extends Sandia’s optimization expertise to real-time application areas.

Packaged Integrated Thin Sensor
141605

Year 2 of 3
Principal Investigator: C. A. Apblett

Project Purpose:
This project endeavors to combine the results of previous investments to produce a functioning sensor prototype that combines power, electronics, packaging, circuit board, and sensors into an integrated platform. The intent is to demonstrate the capability to fabricate a prototype system that retains functionality under the extremes of processing subcomponents and packaging. Previous efforts in this area have been plagued by issues regarding the power source and the electrical interconnects between the circuit board and the die function, as well as sensor-specific ancillary electronics that need to be included in the device. Thus, the majority of the effort in the first year was focused on setting up the issues for these three areas to advance.

While significant advances have been previously demonstrated, the technologies integrated were never demonstrated. The integration is not trivial, and requires significant advancement in the state-of-the-art in interconnects, power sources, and sensor controls in order to demonstrate a system. Innovations in all of these areas would need to be demonstrated prior to moving this component from an R&D environment into an externally funded project, as the maturity and reliability of these devices is relatively low prior to this project.

The goal of this project is to develop a prototypical system that utilizes all of the subcomponent technologies (interconnect, die processing, batteries, sensors, and circuit timing elements) and demonstrates a functioning device that has applicability over a wide range of applications.

Summary of Accomplishments:
We have demonstrated many of the key elements in producing a thin microsystem device. There are roughly three remaining areas that require additional innovation for this program. However, the ability to produce electrical interconnects at low temperature and the ability to integrate thinned devices into the structure have matured significantly. Specifically this year, we have demonstrated the function of the full device at the prototype level without the additional processing (i.e., we are sure that the circuit elements all work together), and we have demonstrated the function of a processed memory chip integrated into the circuit elements. Development of the printed interconnects has taken primary consideration, as the ability to carry signals both at low frequency and high frequency is important to the function of the device. Part of the development of the new circuit has been trying to establish the performance of the printed interconnect at the frequencies of interest, and how the interconnects will interact with the other circuit elements. In addition, a specific new reference clock was designed and built that was compatible with the other circuit elements; these clocks are out of the fab now and are packaged and ready to use. Finally, new battery designs based on the learning done from last year have been developed, and new assembly techniques used that improved the yield of the batteries significantly over the previous year's development. Also, packaging developments have demonstrated that the processes needed to package the systems are compatible with at least some of the circuit elements, although some issues were discovered in the packaging and the die processing and battery packaging.

Significance:
Development of an integrated active radio-frequency identification (RFID) system such as that proposed has significant mission relevance to program offices such as national defense and homeland security efforts. The ability to develop thin, functionally integrated active RFID systems with integrated high-value sensing systems allows for a new ways to provide value added data into these mission spaces, and is in keeping with Sandia's overall mission for improved reliability and enhanced functionality for national security mission space. Each of the technology areas being integrated (interconnect, battery, packaging, clocks, chip processing, and circuit design) help enhance the skillset of available technologies for nuclear weapons and national defense uses. Current leveraging of the technologies developed have already led to Work for Others (WFO) work in this area for specific technologies developed, and we expect additional work based on power source and clocks to be realized. Ultimately, the suite of tools developed in this project becomes the backbone of a technology tradespace in "things thin."

Remote Sensing of Gases for Greenhouse Gas Monitoring and Treaty Verification
141606

Year 2 of 3
Principal Investigator: J. A. Mercier

Project Purpose:
The purpose of the project is to investigate gas filter correlation (GFC) radiometry as a technique for optical remote sensing. Many sensors have absorption features in the shortwave infrared (SWIR) spectral range from 2.0 to 2.5 microns. The major objectives are to model the performance of airborne and space-based GFC imaging radiometers and to design an optical sensor to verify compliance with treaties such as those that might be put in place to regulate greenhouse emissions or possible nuclear proliferation activities.

This work presents several unique challenges. Some of the gases have spectra that consist of very narrow, widely spaced lines. Very high spectral resolution is required to isolate absorption by these lines. Other gases are relatively uniformly distributed around the globe and, therefore, concentrations of these gases must be measured with very high precision in order to draw useful conclusions about local sources. GFC radiometry combines high spectral resolution with high throughput and high signal-to-noise ratio to meet all of these demands. However, scene clutter and interference from water vapor remain as significant issues for this approach. While GFC radiometry has a rich heritage of remote sensing of atmospheric trace gases in the stratosphere and mid-troposphere, the difficulties of working in the SWIR solar reflective range and measuring gases in the lower troposphere have not previously been overcome. By tackling these issues, this project will enable the Rapid Syndrome Validation Project at Sandia to meet mission needs for the DOE and other government organizations.

Summary of Accomplishments:
An initial 1D radiometric model of scene plus sensor that covers absorption bands was developed in MatLab. The major goal of the second and third year is to extend the model to a full 2D, time-varying scene simulation model to better represent both the spectral and temporal signals and noise sources. In order to extend the model, a 3D plume dispersion model is necessary to simulate the contribution from a release source. The 3D dispersion model was refined, using advances in computational fluid dynamics (CFD), as well as visualization and data processing methodologies for analyzing plume dispersal. To that effect, a FUEGO CFD aerosol model for the dispersion of aerosols from a stack under a crosswind has been developed. The model has been used to simulate dispersion of aerosols with light molecular weight. Additionally, a MatLab program has been developed for the measurement of the aerosol concentration across multiple rays that traversed the plume. The rays can emanate from a ground observer or from a sensor in space. This is the first step to integrating the results of the plume dispersion into the radiometric model.

While gas filter correlation radiometry has been used for remote sensing of atmospheric trace gases in the stratosphere and mid-troposphere, it would be a unique application to use the technology as a global facility monitoring technique in the SWIR solar reflective range to measure gases in the lower troposphere. In order to more appropriately characterize the sensor performance against specific facilities, it is important to develop accurate source modeling capabilities. One major success of this research will be to leverage all of the extensive capabilities of FUEGO for detailed mission assessment. FUEGO is a Sandia-developed, massively parallel CFD code that addresses plume transport and mixing at a far finer scale and with far more detail than any existing Gaussian or puff-based transport models.

FUEGO is a 3D, reactive flow code that includes laminar, buoyancy, and turbulent flow models, combustion models, and conjugate heat transfer.

FUEGO includes state-of-the-art turbulence models such as Reynolds-averaged Navier-Stokes (RANS) and large eddy simulation (LES) turbulence models. For the initial plume dispersal calculations, the 3D turbulence and mixing used primarily the dynamic Smagorinsky and time-filtered Navier Stokes (TFNS) models, as they are considered the most adequate. Merging these extensive simulation capabilities with the sensor design expertise within the monitoring systems center will be quite valuable to the remote sensing community.

Significance:
The primary focus of this project is to improve optical remote sensing technology that might be used to verify compliance with treaties such as those that might be put into place to regulate greenhouse emissions or possible nuclear proliferation activities. Space-based operation would allow these measurements to be made globally. These capabilities would be very significant for DOE, NNSA, and the State Department.

Hybrid AI/Cognitive Tactical Behavior Framework for LVC Simulations
141607

Year 2 of 2
Principal Investigator: P. G. Xavier

Project Purpose:
Exploiting its 3D embodied agent simulation technologies, Sandia delivers force-on-force (FOF) simulation-based tools to DoD and other agencies. Using these tools for precision decisions in critical but complex scenarios is intractable because the simulated human entities lack understanding of combat tactics, causing long setup and debugging times. Sandia's live-virtual-constructive (LVC) simulation technology is also applied to FOF challenges. It is a leader in combining live and constructive assets, yet lacks competent, realistic constructive human entities needed for LVC for training, analysis, etc., while reducing the number of people required. Further potential synergy between behavior modeling and LVC systems (e.g., validation and automated model construction) is impeded by lack of scalability in our current LVC framework with respect to constructive entities.

This project seeks to overcome these limitations, especially within tactically intensive 3D scenarios. It will develop, implement, and demonstrate a behavior-modeling framework that builds upon artificial intelligence (AI) and 3D algorithmic approaches and supports appropriate cognitive modeling. This framework will be integrated with physics-based simulation architecture. The result will enable offline analysis, interactive analysis, and LVC-based studies to use the same models and simulation system. At present, this cannot be done because of compromises among real-time behavior, scalability, robustness, and simulation fidelity that we will address.

Such a system will enable each usage mode to produce validation, model development and other results that transfer to the others. To maintain technology leadership while attempting this leap, we take the opposite of the low-risk approach of incremental improvements inside LVC. Instead, the project will extend the capabilities of our cutting-edge, analysis-quality behavior modeling components (e.g., expressive path planning), combine them into a coherent framework, and make it work for LVC. Direct-sponsoring project customers for tactical scenario analysis tend to favor offline analysis, interactive analysis, or LVC-based studies.

Summary of Accomplishments:
We analyzed behavior and LVC simulation component technologies and their interdependencies. We developed a conceptual architecture that seeks to exploit acceptable behavior model element latencies to avoid compromises between behavioral competence and scalability. We hypothesized that this would enable improvement of tactical behavior by generalizing path planning farther and farther beyond finding a shortest waypoint path between a pair of start and goal positions.

- We developed a prototype framework for simulating team behavior. Our initial demonstration showed the feasibility of applying tactical knowledge via a highly configurable path planner to accelerate scenario specification.
- We updated our simulation architecture and path planner to enable asynchronous planning concurrent with interim behavior. We demonstrated use in team behaviors to dynamically update paths in a tactically coordinated way in response to updated perceptions.
- Leveraging previous work on LVC simulation of autonomous robots, sensing, and communication, we produced an integrated demonstration that shows synergy between those LVC elements and the tactical behavior results. The demonstration includes the first integration of our tactical path planning into robot behavior.

- We experimentally studied multithreading the module update loop of the underlying Umbra simulation framework. The results showed the significance of multithreading Umbra worlds, which model interactions, and provide us directions for exploring scalable simulation.
- We developed a new modularity technique that enables large sets of simulated character types and characters with different combinations of behaviors, abilities, resources, etc., without growing the entity class hierarchy.
- We developed a new tactical path planner that provides new, differentiating capabilities for analysis, simulation, and robotics applications. It improves on the generality, expressiveness, modularity, and extensibility of the previous planner.
- We proposed a flexible architecture for character-working memory to meet emerging FOF simulation needs and to enable bridging of cognitive and AI in our simulated humans. We implemented its core.

Significance:
This project developed technology for FOF simulation, training, and analysis tools for tactically intensive scenarios. Such tools are used to enhance our country's warfighting capabilities and to enhance the protection of DOE and DoD assets. We can directly build upon the new path planning capabilities to improve system and mission analysis tools used in our DoD, DOE, and DHS missions.

The new behavior simulation and simulation capabilities can be exploited by new versions of our FOF simulation-based tools, such as Dante, that are applied to our DoD, DOE, and DHS missions. These software results form an S&T springboard that will put focused applied R&D in reach of projects that develop or customize such tools. A flexible architecture for working memory will enable experimentation with memory research theories and results from cognitive science within the contexts of tactical scenarios and LVC simulation.

Solid-State Replacement of Traveling Wave Tubes for Next-Generation SAR
141609

Year 2 of 2
Principal Investigator: R. B. Hurley

Project Purpose:
A limiting factor for miniaturizing radar systems, including synthetic aperture radar (SAR) systems, is the microwave power transmitter, which is located in the final stage of the radar front end before the antenna. Current Sandia-designed systems typically use tube-based technologies, such as traveling wave tube (TWT) or TWT-based microwave power modules (MPM). These tube-based amplifiers have low efficiencies and limited lifetime. The goal of this study is to demonstrate a technology that allows the replacement of TWTs and MPMs with solid-state power amplifiers (SSPAs). If successful, this will improve the reliability, cost, and size of Sandia's SAR applications.

A single solid-state device simply does not have sufficient power necessary for SAR applications (100 watts), but there is potential for combining solid-state devices to reach the 100-watt level. A major drawback to power combining approaches in the past has been that the power available from gallium arsenide (GaAs) devices was so small (only a few watts at Ku-band), that a large number of branches were required to theoretically approach 100 W. Overall output power ultimately became limited by the cumulative loss introduced by each additional branch of power combining; and large number of devices led to a circuit far too complex for reliable operation.

Emerging Gallium Nitride (GaN) devices, however, offer 10 times the power output per device compared to traditional GaAs devices at Ku-band radar frequencies (15-18 GHz). Research-level prototypes are now providing 25 W-30 W in the Ku-band, so 100 watts may be achieved with a handful of devices (i.e., 4-8). The challenge will be power combining these novel devices in a low loss, efficient, and thermally controlled design, and gauging how these devices work when pulsed and combined. How this approach ultimately affects image quality in a high resolution SAR is completely unknown, and must be understood and proven, to allow TWT replacement by SSPAs.

Summary of Accomplishments:
The goal of this project was to demonstrate that emerging GaN solid-state power amplifiers can be used in power combination schemes to produce a viable TWT replacement for airborne radar. The four-device SSPA constructed during this study produced enough peak power at a wide enough bandwidth to form fine resolution SAR imagery at Ku-band. Output power exceeding 30 W was demonstrated with drain efficiencies exceeding 30% at some operating frequencies with negligible power consumption during the off state.

Reduced prime power consumption was achieved using a drain pulsing scheme targeted for SAR applications that did not introduce system-degrading artifacts. Low loss high frequency launches were simulated and implemented in a housing design compatible with a realistic airborne application, providing a baseline design for implementation of future devices as they emerge. A cost-effective, practical approach for providing high radio frequency (RF) circuit and die attachment to a thermally efficient copper-tungsten heat spreader was also successfully implemented.

During the study, viable GaN devices operating at state-of-the-art frequencies in the Ku-band radar allocation were located, implemented and verified for performance over a bandwidth sufficient enough to be useful in wideband SAR applications. The output power achieved from a single GaN device

(~20 W) was 10 times greater than the nearest technologically viable solid-state alternative (i.e., GaAs) at Ku-band radar frequencies. Drain pulsing (and the associated prime power reduction provided by this technique) will be a necessary component of practical active phase array implementation. The design of the pulse modulator for this project is being considered as the baseline for active array development, primarily due to its low off-state power consumption characteristics.

At low duty factors, the operation of the drain-pulsed SSPA appears to be superior to that of a TWT, due to the absence of heater current that is present in the tube. This allows these devices, with the associated gain and bandwidth, to find application in other forms of non-SAR Ku-band radar, especially when lower resolution leads to slightly reduced RF power requirements.

Significance:
A viable Ku-band SSPA with enough power and bandwidth to challenge a TWT in Ku-band SAR applications (as shown in this demonstration) allows scalable architecture options necessary to meet the needs of a diverse number of airborne platforms, from small unmanned aerial vehicles (UAVs) to large manned aircraft. The potential prime power reduction at low duty factors and decrease in volume are attractive for some applications. The 20-W power level demonstrated from even a single GaN device can, even without power combining, find potential use in some near-range, small platform SAR applications. The 30-W four-device SSPA showed that multiple GaN devices can be effectively power combined at Ku-band frequencies to provide usable broadband RF power without degradation in a fine-resolution SAR imaging system. Thus, the demonstration of a Ku-band solid-state amplifier, such as found in this study, furthers the state-of-the-art in radar system design and supplies an option to the radar system designer that was previously unavailable.

Space Payload Flight Software Architecture
141610

Year 2 of 2
Principal Investigator: R. D. Hunt

Project Purpose:
Sandia is currently developing the next generation of space payloads to provide intelligence about worldwide threats to our nation's security. These payloads will utilize new data processing and communication architectures for both flight and ground systems, and new payload software is needed to support them. With high development costs and long development cycles, there is a growing trend to build reconfigurable and reusable systems that have the flexibility and scalability to support new and evolving missions. The payload software must support this trend through a dynamic and reusable design that can support both multi-mission and multi-program paradigms. A design of this magnitude requires a revolutionary approach and will lower the overall software development costs to all programs through code reuse and efficient resource utilization.

The focus of this project is to create a software architecture design for controlling the next generation of Sandia-developed space payloads. It will be based on emerging technologies in both embedded software and communications to create a core set of frameworks, services, and applications that will become the fundamental building blocks of any future payload software. It will complement existing research activities in the areas of node-based flight hardware, mission data processing, sensor development, and ground systems. At this point, many of these technologies are in a draft standard form or have not been demonstrated in space-based embedded systems. Our task is to evaluate these technologies and combine them into a cohesive software design that can operate within the limited resources of space-based embedded systems as well as communicate over radio frequency (RF) links between flight and ground systems. This project allows for a broader perspective of requirements to be considered, a more fundamental and reusable design approach and prepares us to support future programs.

Summary of Accomplishments:
We finished designing the Reference Architecture for Payload Reusable Software (RAPRS) architecture this year and wrote a Software Architecture Description Document (SADD).

We selected the service oriented architecture (SOA) software design pattern to model the architecture. SOA has proven highly successful in corporate computing environments due to their heterogeneous and distributed processing nature. Corporate applications span various departments of a company (HR, Payroll, Travel, etc.) and a SOA allows these applications to seamlessly integrate to complement each other. This environment is similar to the spacecraft payloads built by Sandia. They consist of distributed and potentially heterogeneous processing elements (CPUs, field programmable gate arrays [FPGAs], etc.) running applications that need to share information.

We identified new technologies and techniques that can be used to implement SOA architecture within the resource-limited embedded computing environment of a spacecraft payload. These platforms have a fraction of the computing resources (< 1%) of modern corporate workstations that made this a particularly difficult task. Examples of the technologies include the use of an active object (AO) framework and the data distribution standard (DDS) to create the service framework and enterprise service bus (ESB).

We identified a common set of payload services and documented how they can be implemented to meet the needs of any program. Examples include services that execute commands, collect and report telemetry and distribute time from a common reference source.

Significance:
Sandia's space mission and remote sensing (SMRS) program is an integral part of DOE's nonproliferation programs and the national security mission. To keep pace with new emerging threats, we must continually advance the capabilities of our intelligence systems. This unique software design will help us maximize the capability of future payload data processing architectures and ground systems. It will provide a dynamic capability that allows us to support new and evolving missions. It will also provide a reusable platform to deploy payload applications on, and it will allow us to efficiently use resources between programs.

Tightly Coupled Navigation and Targeting
141611

Year 2 of 2
Principal Investigator: J. T. Spooner

Project Purpose:
In this project, a new tightly coupled navigation and targeting approach will be developed to simultaneously improve pointing accuracy and target trajectory estimation when using multiple spacecraft. While this approach has applications beyond spacecraft, it will be described here in terms of Missile Defense Agency (MDA's) space-based missile trajectory estimation problem. When a spacecraft detects a target, the line of sight (LOS) vector to that target is calculated. The LOS vectors from multiple spacecraft are subsequently fused to form a position and velocity estimate for the target. This estimate is adversely impacted by the errors in the LOS vectors. In this project, the data fusion engine used to create target position and velocity estimates will be expanded to use models of targets and satellite attitudes to globally estimate the LOS of each spacecraft that is contributing measurements. This coupling of the targeting and attitude determination (or more generally navigation) subsystems will enable more accurate target trajectory estimation.

While tightly coupled navigation has been successfully used within global positioning system (GPS)-aided inertial navigation system (INS), the work proposed here is more complicated since many targets and assets of different types need to be considered. If using a standard Kalman filter, this huge number of states will result in a solution that is unable to run in real time. Additionally, the states in the system will continually change as targets/tracks spawn and are later dropped. This approach is different in that a dynamic Kalman filter that considers the sparse nature of its application will be pursued. A previous researcher has proposed using a sparse partitioning approach when a large number of inputs are present. Another researcher has suggested simplifying the covariance calculations by deleting states. In addition to these suggestions, we will consider removing covariance interactions between states to preserve a sparse system.

Summary of Accomplishments:
We developed novel navigation and targeting algorithms suitable for a number of Sandia applications. In particular, we developed a unique approach that uses imagery while staring at earth-based targets that is able to simultaneously determine the target position and estimate errors within an inertial measurement unit on a sensor. In addition, an approach was developed suitable for determining the orbit of satellites (and other orbiting debris) that is very dim. This approach took into account relativistic effects, non-oblate gravity models, atmospheric drag, solar pressure, light time of flight, and lunar/solar gravity perturbations resulting in an accurate orbit prediction tool.

Significance:
Over the years, Sandia has developed world-class satellite payloads. This project is intended to enhance Sandia's capabilities in geolocation and targeting using these and future assets. At the same time, the approaches being developed under this project enable new capabilities in airborne reconnaissance systems for use in homeland security and defense applications.

A Process and Tool Chain for Evaluating Wireless Mobile Devices
141612

Year 2 of 2
Principal Investigator: R. A. Jung

Project Purpose:
The purpose of this project is to create tools to do automated vulnerability analysis of cellular devices. The intent of this project is to deal specifically with two important aspects of the overall research problem. The first is that any automated approach must be flexible in that the market diversity of mobile devices has resulted in thousands of very different embedded systems. The second characteristic defining this research problem is that solutions need to be relatively fast. It often takes months or even years to conduct vulnerability research. This is not acceptable for mobile devices, as the market is moving rapidly and within months or years, devices become obsolete.

This project is leading edge as there is no such capability in existence, commercially or otherwise. It involved a unique combination of research and development available within Sandia.

Summary of Accomplishments:
After several different approaches were explored, the project settled on the overall strategy of standardizing capabilities to external interfaces found on all wireless mobile devices. Several commercial off-the-shelf (COTS) systems were integrated to create understanding of system state during automated vulnerability analysis tests.

The result of this is a vulnerability assessment system that can be used for any 3GPP conforming mobile device. We have demonstrated a real working system in our lab and currently plan to take this research further.

Significance:
This work has positioned Sandia for future work in vulnerability assessment in the mobile phone security arena, a key issue in both civilian and military communications security.

Use of Phase Conjugation in High-Energy Laser Systems
141613

Year 2 of 3
Principal Investigator: D. E. Bliss

Project Purpose:
Systems based on propagating high-energy lasers through the turbulence would benefit from delivering more energy on the receiving elements. Apart from building a bigger laser, higher intensities can be achieved by combining beamlets from multiple sources and correcting for aberrations. Simple methods to combine beams using passive optics (mirrors, splitters) do not ensure mutual coherence, resulting in a beam with a non-ideal wavefront and poor Strehl ratio. Some scientists claim that multiple high-energy laser beams (>100 kJ) can be phase conjugated (PC) and coherently combined by Stimulated Brillouin Scattering (SBS) with an exceptional Strehl ratio. However, the results are not clearly documented in the open literature. If true, these claims would mark a major breakthrough in extending the energy limit for propagating a laser beam and enhance applications relevant to Sandia's mission. In an effort to verify recent claims and develop this technology for Sandia programs, we will investigate PC using a SBS cell and lenslet array similar to a concept discovered through international collaborations. By understanding the trade-off between the maximum attainable energy and best possible wavefront, we will design and field a PC SBS cell that will be tested in both lab and field environments.

The primary goal is to evaluate the low technology readiness level (TRL) concept regarding correcting and combining aberrated high-energy laser beams. The research is not dedicated to a single Sandia program but could benefit several Sandia projects if successful. If results are positive, then future development could be program directed. Successfully achieving the extremely high Strehl ratios claimed by international scientists makes the project high risk. After exhausting research efforts to directly test the foreign designs, we have developed some unique twists based on proven reflective geometries that should improve mutual coherence.

Summary of Accomplishments:
The high pressure SBS cell has been a stable and robust tool in our laboratory for the last year. The cell has held pressure without any recharge. The following summarizes some key insights gained this year.

For a standard SBS geometry with the laser beam focused by a single lens, aberration (heaters) induced tilt (~10^{-3} radian) can be corrected back to the initial pointing stability of the laser (10^{-6} rad) within the measurement error of the far field diagnostic. Previously, we had also measured ~10x improvements in the Strehl ratio by using the SBS process to correct Single Longitudinal Mode (SLM) laser beams in aberrated media. The SBS process can phase conjugate unseeded, non-SLM, laser beams to remove aberration-induced tilt, but higher spatial frequency terms remain uncorrected. The SBS reflectivity is sensitive to differences in the focusable intensity caused by statistical fluctuations of the turbulent aberrations. For the strongest aberrations generated in the laboratory, the SBS reflectivity can vary by a factor of 5x from shot to shot.

The energy threshold for our setup is 13 mJ with no degradation in the PC quality up to 150 mJ. Increasing the laser energy to the Joule level requires some means of decreasing the focusable intensity to avoid laser breakdown. We tested the strategy of using a lenslet array to create multiple lower intensity foci in the cell. Using an array of 10 lenslets, the quality of the SBS return beam was poor, often no better than the aberrated beam. The problem seems to originate with the random phase generated by the SBS process in each individual focus. When the SBS return beam recombines through the lenslet array and into the far field, the random phase creates fluctuating stripes and grid patterns in the beam with no improvement in Strehl ratio.

Our initial results indicate that claims about the effectiveness of SBS phase conjugation with lenslet arrays are probably overstated. However, SBS with a standard geometry in combination with a high gain amplifier medium could still correct large system optical aberrations. If the high gain amplifiers were operated close to saturation, fluctuations in SBS reflectivity would be less important. In the final year of this project, we will guide our experiments to answer these remaining questions.

Significance:

Optical phase conjugation techniques based on SBS are an active area of research. However, significant work is rarely published. True capabilities and objectives are the subject of speculation. An understanding of the capabilities and limits of SBS methods for phase conjugating and combining high energy, short pulse, large, cross-section laser beams will enable Sandia to assess the potential capability and create applications for DOE and Work for Others missions.

First-Principles Prediction of Radio Frequency Directed Energy Effects
151263

Year 1 of 3
Principal Investigator: L. D. Bacon

Project Purpose:
Radio Frequency Directed Energy (RFDE) is demonstrating potential for application in many DoD and DOE mission areas. Systems are being developed for use by at least three services and the DOE. Its acceptance, however, is hampered by the lack of first-principles understanding of RFDE effects on electronics. At present, RFDE mission planning is semi-empirical, done by calculating the incident RFDE fluence and combining that with previously measured levels necessary for producing an effect on the target electronic system. The uncertainty in the details of the electronic systems in modern targets of interest and the very rapid rate of change in the consumer electronics used in these systems make the results from this semi-empirical approach highly perishable at best, or, at worst, irrelevant by the time it is available. Empirical models give us an understanding of what happens with a specific scenario. Naturally, they are limited in how far they can be interpolated or extrapolated beyond the data upon which they are based. What is needed is the ability to predict RFDE effects from first principles, validated against measurements of example systems. First-principles models give us an understanding of why a scenario leads to the results it does. They can be interpolated or extrapolated as far as the physics they are based on remains valid. This ability will allow the details of the target that dominate the response to be identified — something that cannot be done using measurements alone — and their impact on the variability of the response and on effect margins to be addressed. This project will provide that capability as far as it is practicable today.

Summary of Accomplishments:
In FY 2011, we made significant progress in developing first-principles models of coupling to circuit boards with cables. These models included coupling to a single layer board with and without cables attached, and similarly for a board that included a ground plane, allowing us to evaluate the relative impact of cabling in the two cases. The models allowed us to evaluate the impact on coupling and energy distribution on printed circuit boards of dielectric loss and conductor loss, something that is very difficult to separate in measurements. We modeled semiconductor device interaction in multiple ways, including the full-wave electromagnetic parasitic parameters of a diode mounted to a printed circuit board, and a partial differential equation semiconductor physics model of the Spice parameters and the transient high-powered microwave (HPM) response of a bipolar junction transistor as a function of the HPM drive level. We presented an efficient technique for incorporating electromagnetic field coupling into circuit simulation, which should dramatically speed up our ability to explore the impact of uncertainty in the details of the geometry, at the Directed Energy Professional Society Symposium in November and at a mini-conference with the Air Force Research Laboratory Directed Energy Branch in January.

Significance:
The most significant hindrance to using RFDE tools in the DOE national security mission has been uncertainty about its effects and robustness. This first-principles predictive capability will enable the application of RFDE to multiple DOE and DoD mission areas. The Air Force Science Advisory Board has recommended work in this area. We expect interest in the tools we develop from DOE and multiple DoD collaborators.

Multi-Polarization and Change Detection Exploitation of Inverse Synthetic Aperture Radar Data
151264

Year 1 of 3
Principal Investigator: R. Riley

Project Purpose:
Synthetic aperture radars (SARs) perform intelligence, surveillance, reconnaissance (ISR) missions by directly observing signatures of features in a scene containing activities of interest and/or by indirectly observing the evidence of activities of interest via change signatures that are present in multi-collect coherent change detection (CCD) products. The ability to detect activities via the change signatures alone is of great benefit to many applications, and is utilized extensively on existing fielded airborne SAR systems. However, it can be difficult, even intractable, to classify the underlying cause of the change signatures, especially in high-change clutter scenes. Disparate changes from various mechanisms frequently form one contiguous change signature, especially if several hours pass between collections, making it impossible to detect, or discriminate for, the change signatures of interest.

SAR systems already exploit polarimetry to decompose a scene into terrain types, vegetation cover, and presence of man-made objects; however, we are not aware of any application of this decomposition to CCD classification.

This research will investigate the utility of polarimetric-based classification of scene content, as well as changes in underlying polarimetric signatures, to enable change signature discrimination and classification.

Sandia's development radar system will be coupled with an existing dual-polarization X Band antenna gimbal assembly. During the third year of this project, this system will be utilized to collect fully polarimetric phase histories to be used in subsequent polarimetric CCD processing.

If utility of this novel approach to change signature discrimination and classification is observed in collected data, there is significant potential for increased interest in follow-on airborne polarimetric SAR development.

Summary of Accomplishments:
We performed a survey of technical journal articles covering the topic of polarimetric SAR and polarimetric interferometry. Out of this survey, we now understand what the state-of-the-art currently is with respect to the different technology building blocks related to the project objectives.

Using the computational electromagnetics package (CST) we modeled the radiation patterns and associated polarimetric performance of the X Band antenna.

We developed a radar math model to assist in assessing the impact of variations in the antenna pattern polarimetric performance within a SAR scene. This model takes into account geometries on a phase-history-by-phase-history basis, as well as variations in polarimetric response as a function of frequency, and predicts net polarimetric purity (co-pol vs. cross-pol ratios) on a pixel-by-pixel basis. This model allows us to predict ahead of time how much of a test scene should be useable for this study given the modeled, or eventually measured, antenna data.

We performed a multifrequency fully polarimetric near-field scan of the antenna and have compiled these results. Results are similar to what was observed in the simulation, but not identical, which is not an unusual outcome.

We began formulating a construct to assess the relationship between actual polarimetric "information" content and SAR resolution and ambiguities that arise as one increases SAR cross-range resolution. This is an area that has not been addressed to any great extent yet in literature, although there is recent research relevant to this issue associated with the concept of stationary scatterers.

We began formulating a concept for fully polarimetric calibration, with the goal being the ability to perform a calibration correction on an image pixel-by-pixel basis. As part of this study, we also have selected the calibration target that should be utilized to facilitate this calibration concept.

Significance:

If this concept proves to have merit, any intelligence, surveillance, reconnaissance (ISR)/reconnaissance, surveillance, target acquisition (RSTa) collaborators whose observation needs involve utilizing SAR CCD products in scenes where change signatures of interest may be obscured by adjacent/adjoining change signatures of no interest, and where the phenomenology associated with these different change signatures are different, will have strong interest in pursuing this concept for fielded applications.

Furthermore, development of a polarimetric radar platform will also have merit for other national security applications where polarimetry can be exploited, such as end-clutter cancellation for ground moving target indication (GMTI) applications.

Ultrathin Power Systems for Autonomous National Security Applications
151265

Year 1 of 1
Principal Investigator: J. S. Nelson

Project Purpose:
"Things-Thin" devices and technologies require power systems for autonomous operation. Recent advances in thin battery technologies at Sandia not only show promise for thin packaging but also have demonstrated excellent pulse current capability necessary for burst sensor operation, signal processing, and radio frequency (RF) transmission. The ultimate utility of autonomous thin systems is limited, however, by the scant storage capacity of these batteries. A thin energy harvester is clearly needed that extends the operational life of a thin system, thereby removing a roadblock to the adoption of the "things thin" investments. When available, solar or indoor light resources almost always best other energy harvesting schemes — all of which suffer from a need to be coupled to sometimes mechanically esoteric energy sources (heat, bending, vibration). Light is usually available at some point, indoors or outside over a 24-hour period and is, therefore, attractive for non-cooperative trickle charging as well as intentional quick recharge of thin systems.

In this project, we are coupling two innovative advances made recently at Sandia in the area of thin-photovoltaic (PV) cells and thin-film batteries, with available low form-factor charge control circuitry. The thin-PV cells are fabricated using standard silicon or GaAs-based integrated circuit and microelectromechanical system (MEMS) processing techniques, and have achieved greater than 15% efficiency for a 10-micron thick and 200 micron diameter cell. The thin battery technology is based on extensions of existing Sandia cylindrical/button battery cell fabrication materials and technology to direct write film deposition, enabling printed thin film batteries on flexible substrates, and also printing of arbitrary shape (3 mm to 12" square area, 50 mm to 1 cm thickness) 3D batteries. This printing capability has demonstrated printing of functional cells on Kapton and other polymers, by printing the lithium iron phosphate cathode, polymer separator, graphite-based anode, and battery encapsulation polymer.

Summary of Accomplishments:
The primary technical accomplishment in this project is a proof-of-concept demonstration of a thin power system capable of providing long-term operation of small, potentially unobservable "things-thin." This advance will be an enabling technology platform to build upon for a variety of applications of interest to national defense customers. Continued development of the printable battery technology will increase potential applications.

- Ultra-thin charge control circuitry (CCC) designed and fabricated, and performance validated via integration with thin commercial solar cells and batteries.
- Sandia-based ultra-thin solar cell array designed for integration with charge control circuit.
- Sandia-based ultra-thin printable batteries fabricated and tested with CCC. Performance was poor due to battery seal leakage.

Significance:
There is a growing need for large numbers of autonomous, remote sensors for a wide variety of defense and monitoring applications such as environmental monitoring and border security. Many of these sensors require specialized electric power supplies and are located outdoors where solar power is the only continuously available or practical long-term power source. The integrated, thin power system

proposed in this project will provide the necessary charge-recharge capability to realize sustained, unattended operation of these systems.

Ultrathin, Temperature Stable, Low Power Frequency References
151266

Year 1 of 3
Principal Investigator: R. H. Olsson

Project Purpose:
We propose a thin (<100 µm), temperature stable (<2 parts-per-billion [ppb]), low power (<10 mW) frequency reference with crosscutting applicability across Sandia's national defense and nuclear weapons missions. Traditional low noise oscillators are based on vibrations in quartz crystals. While a mature technology, the large size and mounting of quartz crystals presents important mission barriers including: reducing oscillator thickness below 400 µm, ovenizing for maximum temperature stability at low power, and shock induced frequency shifts arising from the large crystal mass. While commercial microelectromechanical systems (MEMS) oscillators are thin and shock tolerant, they utilize weak electrostatic transduction resulting in poor phase noise performance not suitable for communications systems. Recently, Sandia has demonstrated aluminum nitride (AlN) MEMS oscillators with 40 dB lower phase noise than commercial MEMS oscillators. While initial results are promising, the temperature sensitivity, 2 parts-per-million (ppm)/°C, is too high for precision oscillators. The small volume (microresonators are 2 µm thick compared to 100 s of microns for quartz) and substrate isolation (microresonators are suspended above the substrate by narrow beams for acoustic/thermal isolation) provides a new platform for ovenizing oscillators at revolutionary low power levels (<2 mW compared to 1.5 W for quartz). Ovenized oscillators are the gold standard for frequency stability where heaters and temperature sensors are used to maintain the oscillator at a constant temperature above ambient. In this work, we propose to integrate thin film heaters and temperature sensors directly on AlN microresonators to form ovenized oscillators operating from 10-1500 MHz. We will investigate, through modeling and experimentation, ovenized resonators with different anchoring suspensions, heaters, and sensors to minimize oven and circuit power while maintaining resonator performance and maximizing temperature stability. We will implement low power oscillator and oven control electronics, first at the circuit board and later at the integrated circuit level. This project will demonstrate a multifrequency low noise oscillator technology with unprecedented frequency stability over temperature (<2 ppb) at this size and power.

Summary of Accomplishments:
We have developed a thermal equivalent circuit model and a finite element model (FEM) to describe ovenized AlN microresonators of different geometries. Using these models, we have designed, fabricated, and characterized microresonators with integrated ovens and temperature sensors at 600 and 100 MHz. By acoustically isolating the resonator from the oven, quality factors of 2300 (identical to that of non-ovenized resonators) have been achieved. These microresonator designs have demonstrated 65 °C per mW ovenization, allowing the resonator to be thermally stabilized in <3 mW of power, 100 times less than the lowest power ovenized quartz crystal. The measured oven performance demonstrated <10% error from the thermal circuit model and <2% error from the FEM. Based on these models, we discovered that our initial oven designs placed the temperature sensor parallel to the oven, causing a temperature gradient across the sensor resulting in oven temperature drift with changes in ambient temperature. We have designed an ovenization platform upon which a resonator operating at any frequency between 10 MHz and 1.6 GHz can be added. The oven platform features temperature sensors and resonators that have no thermal gradient, making them insensitive to ambient temperature. Oven platforms with resonators from 19 to 500 MHz have been fabricated and are being characterized. We have invented a constant resistance control loop to maintain the resonator temperature. The predicted performance of this control loop is a 4 milli-C change in platform temperature across a –55 to 85 °C

ambient temperature range, corresponding to 4 part per billion shift in resonator frequency. We have designed a printed circuit board (PCB) oscillator with oven control and a single-chip oscillator where both the oscillator electronics and resonator are ovenized for maximum temperature stability. Both the PCB and the single chip oscillators are currently being fabricated.

Significance:

The proposed oscillators are applicable to many small radio-frequency (RF) devices, where quartz has reached a thinning limit and electronics heating of quartz oscillators causes frequency drift, limiting oscillator stability and system performance. By measuring temperature on the microresonator and adjusting the heater current to maintain constant resonator temperature, electronic heating effects are mitigated. The proposed multifrequency oscillators allow for direct frequency synthesis at RF, eliminating power hungry phase locked loops (PLLs) in miniature radios and global positioning system (GPS) receivers. This oscillator technology is applicable to nuclear weapons systems applications, where improvements in vibration sensitivity and reliability are expected.

Efficient Thermal Neutron Detection Using Gadolinium Conversion Layers
151267

Year 1 of 2

Principal Investigator: M. Allen

Project Purpose:
Some types of special nuclear material (SNM) emit both gamma and neutron radiation. Neutron detection is considered a more robust means of determining the presence of SNM for two main reasons: 1) neutrons are more penetrating than the low-energy gamma rays specific to most SNM and 2) there are fewer natural and man-made sources of neutron radiation, which makes the detection of neutrons more significant. Helium-three (He-3) gas-filled tubes are ubiquitous for thermal neutron detection High efficiency and low sensitivity to gamma radiation have made He-3 tubes the neutron detector of choice for decades. However, He-3 is increasingly scarce and expensive to acquire due to a recent increase in demand and its very limited production. Therefore, new efficient neutron detection technologies are urgently needed.

We propose to develop a thermal neutron detector based on materials that have high probability of absorbing neutrons and then emitting energetic electrons. Gadolinium (Gd) has a very high neutron absorption cross-section, and emits energetic "conversion" electrons following neutron absorption. The emitted electrons have energies ranging from tens to hundreds of kilo-electron volts (keV) and are emitted (at various energies) up to 60% of the time following neutron capture. The measured electron signal produced from such a detector will be directly proportional to the incident neutron flux. Due to the high neutron-absorption cross-section and internal conversion coefficient of Gd, 30 – 40% intrinsic efficiencies are possible. Furthermore, this solid-state detector should be scalable to large areas to achieve a high absolute efficiency. The development of a successful prototype will require creative integration of several identified phenomena. Conversion electrons have moderate energy and are difficult to measure. The ability to discriminate thermal neutrons from other radiation sources will require integrating various technologies to collect, focus, amplify, and analyze conversion electrons.

Summary of Accomplishments:
We successfully measured conversion electrons produced from neutron capture in a gadolinium foil. The conversion electron emission from a range of foil thickness from 3 microns to 20 microns was measured. We found that a gadolinium foil thickness of approximately 7 microns — the corresponding to one mean free path of a thermal neutron in natural gadolinium — was optimal for capturing neutrons while still allowing the escape of energetic electrons. Simulation work using the Monte Carlo radiation transport code GEANT4 is progressing. These simulation results and computational modeling capability will be of great value when we begin to model methods of electron transport, collection, and amplification as discussed in the section of our proposed work for FY 2012.

Significance:
The detection of thermal neutrons is necessary to a broad range of national security and nonproliferation missions. DOE’s recently released Radiation Sensors and Sources Roadmap for 2010 (NA22-OPD-01-2010) lists large-area thermal neutron sensors as both high priority and high impact. Such neutron detectors (either large area or portable) would potentially benefit other organizations within NNSA that conduct nonproliferation treaty and compliance and verification missions, as well as for DHS applications.

Cryogenic FPA Optical Interconnects
151269

Year 1 of 2
Principal Investigator: A. Y. Hsu

Project Purpose:
Next-generation satellite-based imaging systems will require focal plane arrays (FPAs) with higher pixel number and faster frame rates, driving the need for higher-bandwidth data interconnects to transfer data from the FPA. Optical interconnects over fiber have the advantages of scalable bandwidth (>2Gb/s/ch), and reduced size, weight (>10x reduction in cables) and power consumption (10x reduction) compared to electrical interconnects. For short-wave-infrared and mid-wave-infrared FPAs, cryogenic cooling (to <120K) is typically required. To date, cryogenic optical interconnects have not been demonstrated for data transfer directly from an FPA motherboard.

The project will develop and integrate several unique technology elements that will be required for this application. Specifically, they include:

- Three new vertical-cavity surface-emitting laser (VCSEL) technologies will be developed to achieve a low-power, high-bandwidth laser that operates at both 105 K and 300 K: higher bandwidth InGaAs quantum wells, lasers that operate from the n=2 quantum transition at 300 K, and intra-cavity electrical contacts. Theoretical predictions support these new device technologies, but none have been experimentally established at Sandia and they are expected to be challenging and risky.
- Design, modeling and development of robust cryogenic mechanical and optical packaging for temperatures between 105K and 300 K, employing novel microfabrication processes typically used for creating integrated circuits.
- Integration of the VCSEL optical package, a previously developed Stanford serializer/driver integrated circuit (IC), and interface with an FPA read-out integration circuit (ROIC) that generates the input electrical signals for the optical transmitter. After integration, an interconnect demonstration will be conducted at 105 K, with optical signals received by a commercial photodetector/demultiplexer to show error-free transmission at 4Gb/s.

Summary of Accomplishments:
VCSEL Development:
Design, growth, fabrication, and characterization of low-temperature-operating (T=105 K) InGaAs VCSELs with low threshold current and 2mW optical output power at 120 K. Good laser performance was measured down to the T=105 K which is the limit of the current measurement setup.

- Description of 300 K and 105 K performance and comparison with expectations from n=2 design
- Small-signal modulation bandwidth of >10GHz at room temperature has been measured which is expected to exceed high-speed demo needs.
- Open-eye diagrams were measured at 300 K & 105 K at 2.5Gb/s data rate. Operation up to 5Gb/s is predicted based on measured rise/fall times.

Low-Temperature Optical Packaging Development:

- Designed and modeled a robust optoelectronic package suitable for cryogenic operation and began microfabrication of key components. 3D finite-element modeling of the athermal design shows negligible movement and stress across the wide operating temperature range (100 K to 300 K).
- Optimized the VCSEL/microlens/fiber optical design by raytracing methods, with the finalized structure expected to achieve >95% coupling efficiency and several microns of alignment tolerance.

- Investigated new microfabrication processes to allow the creation of custom refractive microlens components in the Microsystems and Engineering Sciences Applications (MESA) facility. A design of experiments was used to systematically explore the impact of plasma conditions on fused silica etching.
- Performed measurements of etched lenses, which showed coupling efficiencies of >90% without the use of anti-reflection coatings and focused spot sizes of 30 microns, both in excellent agreement with theory.

System Demo Development:

- Designed a custom circuit board to facilitate the evaluation of a high speed (3.36 GHz) COTS clock multiplier chip (ADC4350) at cryogenic temperatures with ability for testing of the Clock multiplier chip and Stanford serializer separately and together, 160 MHz in, and 8 b10 b data out.
- Initial round of cryogenic testing revealed that the ADC4350 operates down to 55 K (–218 °C), and successfully operated continuously for >150 hours (test stopped).

Significance:
We are working to develop new remote sensing systems for DOE and DoD applications. The performance of many of these systems is limited by present state-of-the-art in focal plane array technology. Advances in FPA architectures, which enable high data throughput rates with reduced weight and power constraints, could enable a wider proliferation of sensors as integration impacts are eased. Systems employing optical fiber directly off the FPA will enable higher frame rates from larger FPAs while still reducing host space vehicle integration impacts.

Trusted Software Architecture for Multi-Processor Embedded Computing
151270

Year 1 of 3
Principal Investigator: K. Robbins

Project Purpose:
Cyber warfare targeting military systems from adversaries and nation states is an increasing concern. Examples of this include cyber-espionage, data intrusion/interception, subversion, malware, denial of service, hardware/software Trojan horses, spoofing, jamming, and network attacks. Currently most cyber security initiatives primarily focus on nonspace systems such as those for weapons and terrestrial systems.

Developing a trusted software architecture for space-based systems is complicated by unique characteristics of the flight segment, including a legacy flight software heritage largely ignorant of security concerns; the inability to access or recover flight hardware once placed in service; size, weight, and power constraints; and the inherent nature of remote command/control and large data collection.

We will address the challenges of developing trusted software architecture for space-based systems by co-designing a new execution framework for flight applications and a fully integrated security architecture that leverages Sandia's cyber security expertise to meet the specific security concerns of these systems.

The execution framework will provide the capabilities needed to manage flight software applications on next-generation node-based reconfigurable processing architectures, including the facilities to manage the flight hardware, deploy and configure applications, monitor the system and applications for anomalous behavior, and detect/recover from failures. We will research, develop, and demonstrate automated deployment/configuration algorithms to “place-and-route” or assign software components — the basic building blocks of applications — to available processing nodes subject to power, performance, and reliability constraints.

Given the central role this execution framework will have in future space-based systems, it is critical that the security architecture be an integral part of its development. We propose to research and develop a security architecture primarily focused on protecting the flight payload architecture. Efforts will focus on methods to enhance cyber-security of data processing modules, pointing and control, and data downlink from design to deployment. We will look at including trust anchors in the payload that will detect and prevent such attacks.

Summary of Accomplishments:
- Analyzed, designed, and tested event-driven actor framework: demonstrated both on Linux workstation “nodes” and on testbed of Xilinx ML507 development boards configured as joint architecture standard (JAS) cluster head nodes.
- Designed and demonstrated “Dining Philosophers” mission application that shows all essential characteristics of distributed publish/subscribe–based mission applications supported by the payload operating system.
- Developed meta-models for payloads and mission applications that simplify designing and implementing the Deployment Planner and support developing domain-specific modeling tools.
- Designed/implemented initial Deployment Planner that identifies a deployment plan statically at system start-up.

- Designed/implemented prototypes of Payload Gateway, Node Agent, and Node Manager components of the payload operating system.
- Designed/implemented a visualization (and control) framework that enables rapid construction of visualizations and test benches for TEMPOS applications.
- Developed a portable operating system interface (POSIX) socket interface to Gaisler SpaceWire driver.
- Ported OpenSpliceDDS (publish/subscribe middleware) to Gaisler Linux on Leon3/SpaceWire platform (ML507 development boards).
- Analyzed candidate software security mechanisms (security functionality deployed in the run-time system).
- Analyzed initial candidate hardware security mechanisms.
- Designed draft payload reference model to support eventual s.ecurity assessment of the TEMPOS hardware/software architecture.
- Established project development infrastructure: configuration management system, software tool chains, unit/integration test frameworks, build management, continuous integration server, software static analysis tools, etc.

Significance:
Sandia's Space Mission and Remote Sensing (SMRS) program is an integral part of DOE's nonproliferation programs and the national security mission. This program is a key national asset to provide intelligence about worldwide threats to our nation's security. To keep pace with new emerging threats, we must continually advance the capabilities of our intelligence systems. This work will demonstrate methods of software construction that realize the full potential of node-based hardware architectures in development, including the JAS. These methods will greatly improve Sandia's ability to reuse software across programs and to enhance software functionality throughout the mission.

The Birth and Death of Topics
151272

Year 1 of 1
Principal Investigator: A. T. Wilson

Project Purpose:
Although recent advances in topic modeling algorithms such as latent Dirichlet allocation (LDA) have greatly advanced our ability to rapidly summarize and comprehend large collections of documents, nearly all the algorithms —including those that try to model topic evolution — share one critical shortcoming: the closed-world assumption that the number of topics and the vocabulary do not change over time. This is a problem when analyzing real-world corpora where topics evolve, emerge, split, recombine and disappear.

Rolling back this assumption enables one gigantic 'aha' moment: the ability to detect automatically a sudden change of subject (or the emergence of new subjects) in a dynamic corpus of documents, even when the new topic is completely unknown a priori. It also enables capabilities such as dynamic sentiment tracking where an analyst needs to track people's opinions on various topics based on their writing; or network threat detection using Web traffic, email headers, or protocol logs as documents.

This extension also provides a clean mathematical way to present what is different in a collection of documents at two different times — not just the difference proportions of topics but also what has newly emerged and what has dropped out of sight.

The Bayesian formulation at the heart of LDA's topic discovery suggests an approach based on Bayesian birth/death processes similar to those used in queuing theory. Briefly, at any time t, any topic z has a chance of dying out or of fragmenting into two sub-topics in time t+1. Our principal task is to model these probabilities in a way that plausibly imitates what we see in real-world corpora.

Nearly all extant LDA-based models require the user to choose the number of topics a priori and hold it fixed through time. Our innovation work will break new ground by removing this limit.

Summary of Accomplishments:
We designed, implemented, and demonstrated an unsupervised algorithm that discovers new topics in an evolving stream of documents. It operates on the intuition that, while the vocabulary in a conversation drifts naturally over time, a sudden shift in language is likely to herald a new subject of discussion. We formalize this concept by appealing to the notion that topics in LDA are probability distributions. We then measure drift using Jensen-Shannon divergence, a convenient measure of divergence (drift) between distributions.

We demonstrated our algorithm on sets of articles from a blog focusing on popular culture, science fiction, copyright, and intellectual property. Our approach was able to detect and identify, for example, major events in 2005 including Hurricane Katrina, conditions in the Astrodome immediately following the hurricane, and high-profile lawsuits against Apple and Sony regarding copy protection.

By designing our algorithm as a modification of an existing technique LDA, we have made it straightforward to incorporate speed enhancements for LDA that have been developed in recent years. Most notably, we will be able to re-use the ParaText parallel LDA framework instead of having to begin an implementation from scratch. This will allow our algorithm to run on platforms from a laptop all the way up to hundreds of cores on Red Sky — a scale large enough to handle tens of millions of documents.

We learned that detecting the death of topics is less straightforward than identifying their birth. Since LDA is built on stochastic (random) sampling, it will almost never eliminate a topic entirely. We observe instead that expiring topics dwindle to some minimal volume and cease to become meaningful. Time constraints kept us from pursuing that observation further.

Overall, we accomplished our goal of detecting without supervision the emergence of new topics in document sets.

Significance:
One main part of an analyst's job is to assess a large amount of information, compare it with the way the world was yesterday, and identify the differences. Much of the art of being an analyst consists in managing the avalanche of information. Our work is a force multiplier that distills content to indicate what topics changed, where those changes manifest, and when the changes happened. This frees the analyst to concentrate on why and how things changed. By targeting such a basic task, our work will have broad applicability across many agencies.

Matterwave Interferometer for Seismic Sensing and Inertial Navigation
151275

Year 1 of 3
Principal Investigator: G. Biedermann

Project Purpose:
In recent years, the performance of inertial navigation systems has reached a plateau due to the limits of available sensor technology. Light-pulse matterwave interferometry is widely recognized to be the next advance for inertial measurements. Demonstrations measure both rotations and accelerations with outstanding fidelity, stability, and intrinsic accuracy. In seismic sensing, a six-axis matterwave sensor can potentially discriminate between and characterize natural and manmade sources in new ways as well as independently infer wave speed and direction to reduce event location uncertainty. Current atom interferometers are large, delicate, bandwidth-limited to a few Hz and untenable for rugged seismic and navigation applications. We propose a tabletop demonstration of the first high-bandwidth (100 Hz) matterwave gyroscope/accelerometer that may enable a broadband and reasonably rugged device. We will evaluate this technology with input from in-house experts in both the navigation and seismology user community to lay groundwork for a full system development program.

We will operate the interferometer in a new short time-of-flight regime enabling a small 10 cc physics package. We anticipate two orders of magnitude gain in data rate and new opportunities for reductions in size and system requirements. A new property of this approach, heretofore unseen with matterwave sensors, is that the orientation can, in principle, be rotated with respect to gravity without severely affecting the performance. Using two counter-propagating interferometers, we can simultaneously measure accelerations and rotations using a new technique of rapid exchange between two spatially separated atom traps. During the short ~10 ms free flight between traps, a light pulse atom interferometer sequence determines the platform rotation rate and acceleration with respect to the pristine atom proof mass. We forecast that within a few years this concept can achieve sensitivities of 10 nano-g/rtHz for accelerations and 12 nano-rad/s/rtHz (42 micro-deg/rthr) for rotations.

Summary of Accomplishments:
An apparatus to cool and directly control neutral Rb 87 atoms was designed and created. The full apparatus system consists of multiple laser systems, laser locking equipment, control software, a magneto-optical trap, and a vacuum vapor cell. The system allows for the trapping of a cloud containing approximately one million atoms, with a diameter on the order of 1 millimeter in diameter, and can cool the atom cloud to a temperature of 5.5 micro Kelvin. Additionally, through the use of stimulated Raman transitions, we can coherently manipulate the electronic state of the atoms in the cloud, allowing us to implement operations such as atomic beamspitters and atomic mirrors.

We have used this system to demonstrate an atom interferometer accelerometer (AIA) that operates at data collection rates between 50 Hz and 330 Hz with sensitivities from 0.57 micro-g/rtHz to 36.7 micro-g/rtHz, respectively. These sensitivities are comparable to the sensitivities of many other AIA demonstrations, yet all other AIA have operated at a few Hertz or less. The combination of operating at high data rates with good sensitivity demonstrates a path to new applications in highly dynamic environments such as inertial navigation and seismic studies.

The performance of the device can largely be attributed to high recapture efficiency of atoms from one interferometer cycle to another, which ranged from 95 to 85%, depending on operating rate. Previous AIA demonstrations relied primarily on capturing atoms from background vapor to repopulate the cloud from cycle to cycle. By recapturing the dense cloud, the time necessary to accumulate a cloud having a large atom number is drastically reduced, allowing for much shorter interferometric cycle times. A technical advance concerning this method was written and accepted, and a provisional patent application has been submitted.

Significance:
The development of atom interferometer sensors has high technical risk with potential for significant payoff for the scientific and application communities. Federal agencies such as Office of Naval Research (ONR), National Geospatial-Intelligence Agency (NGA), Defense Advanced Research Projects Agency (DARPA), Air Force Office of Scientific Research (AFOSR), and Army Research Laboratory (ARL) have demonstrated their interest by ongoing investments in this technology. Applications relying on inertial measurement units will leap ahead in capability due to the revolutionary performance of atom interferometers. This is a demonstrated sensor technology with an enormous application space to national security.

Spectro-Temporal Data Application and Exploitation
151276

Year 1 of 3
Principal Investigator: J. K. Roskovensky

Project Purpose:
This effort will focus on assessing mission capabilities of new state-of-the-art sensors that were designed and produced to acquire unique spectro-temporal data from space. Rigorous end-to-end sensor/data/product characterization will focus on three separate R&D sensor components: a visible prism, a set of visible band polarization filters, and a short-wave infrared (SWIR) phase grating. These components were designed as R&D instruments to provide unique data collection opportunities alongside well understood multispectral data. It is strongly believed that these sensor components may not only provide greater information of standard collected targets, but the ability to broaden the future national security target and mission space tremendously. However, they also pose a significant challenge for data analysis and interpretation. The expansion of the number of variables and dimensionality of the data geometrically increase the data analysis requirements.

There is a large amount of uncertainty in the behavior of the sensor and the quality of the resulting data of these R&D components. A great deal of work still has to be performed in order to understand the potential data products and their utility. Several cutting-edge technical aspects that are applicable to this work provide a high probability of successful outcomes. New polarization atmospheric radiative transfer codes are being integrated into radiometric scene simulation codes for accurate modeling of target reflected polarized light. Laboratory sensor test data, largely analyzed only for functionality, are expected to provide a means to perform novel sensor characterization. Finally, newly developed multiway algorithms, that have been shown to extract complex information from hyperspectral image datasets will be improved and adapted for analysis of data from these innovative sensors.

Summary of Accomplishments:
The results for the first year:
Scene Modeling:

- Commencement of polarization filter data
- Simulations useful for Prism analysis
- New scene development that includes seasonal changes, and urban and road infrastructure

Sensor characterization and modeling:

- Optical spectral point spread functions (PSFs) determined for 0th and 1st order grating sensor as well as for the Prism sensor for on-axis and four off-axis field angles
- Complete grating sensor model developed that includes optical, focal plane array (FPA), and dispersion properties that compares well to collected data with limited calibration thus far
- Modeled data of various targets has been produced for mission analysis purposes

Data analysis:

- Initial analysis efforts have been made to extract and assess the spectral target information. This effort is in its preliminary stage.
- Specific through-focus collections with both the grating and prism were made to aid the sensor characterization and modeling efforts

Algorithm Development:

- High-dimensional data algorithms were tested on test data, “real” data, and synthetic data of the grating sensor
- Principal components were used to find bad pixels
- PARAFAC algorithm was able to determine multimodal temperature states in spectral signatures
- Recent examination of temporally changing signatures has begun

Mission assessment: Field angle effects of the grating sensor were evaluated that showed spectral integrity was maintained. Temperature retrieval from modeled data was demonstrated using PARAllel FACtor analysis (PARAFAC) algorithm. Atmospheric effects were assessed and showed to be quantifiable. Initial efforts indicate that grating data will be useful for simultaneous target temperature while estimating atmospheric water vapor columns values. Grating spectra has initially been shown to provide specific characterization and typing of highly spectral absorption features from certain important molecules contained in interesting targets.

Significance:

The intent of this effort is to develop mission capability that would be applicable to the nation’s present and future space systems and would provide the end user community with novel capabilities in support of national security, economic, and environmental interests. Identification of various trace gases in the atmosphere would benefit sectors of the DOE and new environmental capabilities from national systems could provide data for groups interested in climate analysis.

Adaptive Automation for Supervisory Control of Streaming Sensors
151277

Year 1 of 3
Principal Investigator: J. H. Ganter

Project Purpose:
National intelligence and security depend on effective remote sensing, the acquisition of knowledge from a distance using instruments that transform energy into information. Sandia remote sensors include the multispectral thermal imager (MTI) and synthetic aperture radar (SAR) aboard unmanned aerial vehicles (UAVs).

To improve the performance and utility of remote sensors, Sandia recently conducted studies of human labor demands located downstream of the sensing instruments. In the ground processing stage, signal processing algorithms running on large computing clusters detect signatures in noise and classify signatures into target categories. But there is a surprisingly large, and even growing, reliance on human experts to tune the algorithms to user needs, mission goals, and evolving situations. The next generation of sensors will change a labor shortage to a labor crisis. Manual labor has become the primary limiting factor in both technology rollout to national security missions and R&D investment in new sensors. To solve the sensor labor crisis, we need a new parallel to the autopilot that has become ubiquitous aboard aircraft and ships. This trusted and powerful machine aid will free human time and attention for tasks people do well. These skilled tasks include situational awareness, situational understanding, and the making of difficult choices among options. This project will invent a sensor autopilot by hybridizing methods from statistics, signal processing, control theory, and cognitive systems.

A sensor autopilot must solve problems that are underspecified and thus dramatically more difficult than typical control problems. Probability density functions (histograms) of both targets and backgrounds are noisy, unknown a-priori, and evolving. Solutions must be numerically generated very rapidly to remain within the time constant of the sensor control loop. We believe that creatively blending adaptive signal processing with control theory, human-supervised training, and machine learning could solve many problems currently limited by human operator bandwidth.

Summary of Accomplishments:
- Extended the SIMAT MatLab simulator to incorporate a simple feedback loop to control the rate of threshold exceedances
- Discovered that areas of high spatial gradient have a large effect on local threshold exceedances, thus motivating the development of noise models
- Analyzed sample data to characterize noise distributions and begin to break out independent sources rather than lumping them together
- Modified Scene Kinetics Mitigation (SKM) to produce a jitter signal
- Conceived of treating gain and threshold separately
- Began MatLab experiments in target tracking

Significance:
Military leaders express increasing concern about the growing labor footprint of high-speed, high-resolution sensor systems. Sensors that can be built but not staffed will fall short of their technical potential. With this project, Sandia will take the first steps in an industrial revolution that solves the labor crisis of advanced sensors. If successful, Autopilot has high potential for DOE nonproliferation and DoD tactical and strategic sensors applications.

Phase Diversity for Advanced Systems
151278

Year 1 of 2
Principal Investigator: E. A. Shields

Project Purpose:
Due to limitations in manufacturing and alignment, all imaging systems exhibit an inherent amount of optical aberration that degrades performance. For orbital systems, these quasi-static aberrations are compounded by misalignments induced by gravity release and dynamic thermal loads that cause changes to the metering structure, directly distort optical surfaces, and alter refractive characteristics of lenses. These combined effects can severely degrade imaging performance.

Sandia's current techniques for compensating for these effects on-orbit include piston actuation of mirrors and heating of lens groups to implement desired focal changes. These approaches are calibrated with star images (requiring periodic re-pointing), are susceptible to hardware failure, and exhibit limited utility in addressing aberrations other than defocus. Other approaches for correcting optical aberrations utilize wavefront-sensing techniques and actuated deformable mirrors. These architectures require a significant number of additional optics and greatly increase system complexity and risk.

Phase diversity (PD) is an image-processing technique that operates on a collection of defocused images of a specific scene. The ensemble of defocused images and known defocus values are used to reconstruct the unaberrated scene and the wavefront aberrations of the imaging system.

PD has successfully been applied to imaging systems with limited fields-of-view (FOV) over narrow spectral bands. Yet, theoretical development has not addressed issues of field-dependent aberrations inherent in systems with larger FOV. Algorithms that can accommodate wavelength-dependent aberrations in scenes with broad spectral content have also largely been ignored.

For broadband terrestrial imaging systems, aberration content across the FOV and spectral bandwidth can vary significantly. The effects of these aberrations are convolved in the collected panchromatic imagery, complicating the problem of separability and image recovery. An innovative approach to including these dependencies in the algorithm itself can enable application of PD image enhancement to wide-field earth surveillance missions.

Summary of Accomplishments:
Significant gains were made in the creation and development of a polychromatic, phase-diverse phase-retrieval algorithm. We showed that when imaging a point source of known spectral content, the wavefront as a function of wavelength could be reconstructed.

Code was written that allows this algorithm to be tested and explored. We have begun to utilize this code to explore the usefulness of this algorithm to real-world systems. The test case used wavefront errors at different wavelengths that were uncorrelated. Also, only a finite number of wavelengths were used in the simulation. We have begun to explore the impact of using aberration content from real-world systems as well as using more wavelengths in the simulation than the reconstruction (thereby more closely matching a true broadband system).

Code for a scene-based phase-diversity algorithm was written and demonstrated to function well. This is a traditional algorithm that works over a narrow field of view. This algorithm will form the basis of our effort for including field-dependent aberrations into the phase-diversity algorithm.

We have designed and procured equipment for a phase diversity test bed. This testbed will allow us to demonstrate the utility of algorithms developed in a real-world environment with measured, rather than simulated, data.

Significance:

The results of this project could be used to aid in the assembly, alignment, modeling, and characterization of optical systems. Phase diversity algorithms could be used at various stages of system integration to provide useful data that may not otherwise be available. Examples could include:

- Component-level testing could be conducted in new and novel methods not subject to the limitations of traditional interferometric testing.
- Small R&D programs without schedule or budget for interferometric testing often still must use through-focus point-spread function measurements to correctly position the focal plane arrays. Results of this project could allow these data to be used for wavefront measurement as well, thereby providing increased understanding, characterization, and modeling capabilities for the optical system.
- Integration of focal plane arrays precludes interferometric testing, but the algorithms developed as part of this project would allow wavefront measurements to be collected with the focal plane arrays installed. This allows for testing much later in the integration cycle, thereby helping optical engineers better understand system performance.
- Interferometers are not always available at the wavelength of interest. This project would allow wavefront testing at any wavelength(s) to which the focal plane array is sensitive.

Furthermore, this project could open the door for new missions for Sandia's systems. The polychromatic, phase-diverse phase-retrieval algorithm could allow for multispectral data to be obtained with panchromatic imaging systems. Systems that now simply characterize the brightness of a spot could then be used to also characterize the source's spectral content.

The wide-field phase diversity algorithm could be implemented to better characterize and improve system performance for a variety of Sandia systems. The characterization of wavefront variation as a function of field provides useful information for optical engineers responsible for understanding and modeling system performance. This knowledge allows for higher-resolution images to be created, thereby improving mission utility.

Novel Signal Transmission and Intercept Methods Using Applied Information Theory and COTS Radios
151283

Year 1 of 2
Principal Investigator: A. Ferguson

Project Purpose:
There is an ever-evolving need for novel, long-range, covert radio communications within the tagging, tracking, and locating community — as well as by US government agencies with national security related missions. This need applies to existing products and infrastructure and extends to the requirements of next-generation products as well. Previous research efforts have shown that non-coherent, add-on processing can greatly increase the link margin of low power commercial off-the-shelf (COTS) transceiver chips in proprietary applications and, at the same time, provide low profile waveforms. The added link margin can be used to form symmetric hardware architectures, increase range of communication, penetrate harder target environments (like foliage and/or hardened facilities), or more importantly, adjust waveform characteristics to hide the communications signal. This project will identify and adapt additional "add-on" processing methods uniquely applied to more common COTS radio hardware such as 802.11, wireless universal serial bus (USB), or Bluetooth. The result of this effort will provide a method for enhanced use of existing infrastructure and "common" radios. Long range, covert communications will be demonstrated without making hardware modifications to the radios.

Summary of Accomplishments:
The following are the key achievements of the effort:
- Designed ability to inject our own signaling
- Deigned ability to create novel protocol enhancement
- Designed ability to produce and receive novel signaling
- Designed ability to add novel sequences and perform enhanced correlation techniques
- Designed ability to perform symmetric point-to-point, point- to multipoint communications.
- Designed ability to analytically evaluate signal strength
- Designed ability to perform novel directional reception techniques

Significance:
The work will help to position Sandia with the unique capability of communicating low profile waveforms from unmodified, standard off-the-shelf products in a covert manner over longer ranges. This concept can directly assist US government agencies with national security related missions, in the design and development of communications systems where low probability of detection is critical. If successful, this strategy would be applicable to customers within the intelligence community.

Command Intent on the Future Battlefield: One-to-Many Unmanned System Control
151285

Year 1 of 3
Principal Investigator: S. Buerger

Project Purpose:
The DoD faces a looming crisis in the control of unmanned systems (UMS). Acquisition trends driven by Congressional mandates ensure that forces will continue to un-man. Today's multiple-operator-per-vehicle remote control methods will scale neither to meet the needs of a cost-conscious security establishment in which manpower is the single largest cost driver, nor to accomplish effective, centrally commanded operations involving tens to hundreds of heterogeneous unmanned assets working together in the same battle space. DoD leaders are recognizing that in predominantly unmanned conflict, intelligent, coordinated, man-in-loop control of multiple UMS will be the key differentiating technology. Previous approaches to multiple UMS control have worked toward an ideal of pure autonomy, but to adopt autonomous control systems for potentially lethal assets would require certain perfection in algorithms. Instead, we envision one-operator-to-many-asset control systems that compensate for perpetual imperfection in control algorithms by keeping human commanders in total control in real-time while making units of heterogeneous unmanned assets as responsive to command intent as platoons of soldiers. This project will be directed toward demonstrating several high-risk aspects of our vision to enable a long-term future of predominately unmanned combat. First, heterogeneous assets will be made to share missions by dividing tasks at a higher level of mission abstraction than current research permits. This effort will be based on existing “collective control” capabilities but will create a new capability to enable the use of heterogeneous assets (e.g., air and ground vehicles, ground sensors) for complex shared tasks. Second, the control structure will be hybridized to allow real-time human command shaping of mission execution. Continuous human input will not only provide specific means of compensating for algorithmic imperfections, it will also provide support to unmanned assets in difficult situations (e.g., in navigating difficult patches of terrain). Progress will be marked by multi-asset hardware demonstrations.

Summary of Accomplishments:
We have demonstrated the extension of collective control algorithms and the application of particular optimal control approaches to mission sharing by heterogeneous assets. We have validated two different approaches in simulation for a variety of mission behaviors and shown that these methods can take advantage of heterogeneity among assets.

We have developed and implemented a test and demonstration platform consisting of several heterogeneous ground vehicles and an asset representative of an aerial vehicle. We have used the UMBRA simulation framework software environment to integrate the system and to enable control via MatLab. We have used the open-source Robot Operating System to control the mobile assets, allowing us to take advantage of open-source tools that have been previously developed by others. The system allows teleoperation and autonomous control of the various assets and provides a rich and meaningful display to the operator.

We have implemented our control algorithms on the hardware testbed, running initial experiments to validate simulations. We continue to refine this implementation to improve performance.

Significance:
While UMS have undoubtedly succeeded in saving lives, manpower needs have only increased. Giving one operator the ability to control many UMS could reduce cost and improve tactical effectiveness in a military increasingly composed of unmanned assets. The mission to protect borders (by DHS), government facilities and other secure sites, including those that house high-value DOE assets, faces similar manpower challenges and evolving threats. Cost savings could be realized by applying the work results to enable one remote operator, protected in a secure site, to replace several security police officers on a perimeter with multiple UMS.

Multi-Mission Software-Defined RF Spectrum Processing
151286

Year 1 of 3
Principal Investigator: P. E. Sholander

Project Purpose:
The military's migration to network-centric warfare requires a robust set of airborne sensors that are directly taskable by unit commanders. For cost and complexity reasons, these sensors will be (size, weight, and power) SWaP-constrained and flown on unmanned aerial vehicles (UAVs). These multi-mission unmanned aerial systems (UAS) will enable novel system-level applications and concepts of operations (CONOPS) via wideband "software-defined spectrum processing" (SDSP) that support a range of surveillance (e.g., synthetic aperture radar [SAR]) and communications missions. For example, multiple, cooperating, SDSP-enabled UAS could improve communications within urban terrain and other challenging environments. They could also provide an organic high-data-rate link for SAR imagery download to a ground control station (GCS) and, thereby, enable a flexible partitioning between airborne- and ground-based processing. An enhanced communications capability between UAS could enable multi-static SAR capabilities and the exchange of baseline change-detection data. More generally, a flexible SDSP system that could receive, digitize, and process 300-500 MHz chunks of spectrum while being swept (over several seconds) through the frequency range of several hundred MHz to several GHz would support a wide range of Sandia missions. While wideband SDSP systems present significant computational and signal processing challenges, there are also significant challenges in the designs of the antennas, radio frequency (RF) front ends, and initial spectrum digitization. This project will focus on SDSP hardware design and implementation and the novel CONOPS enabled by a multi-mission SDSP capability. A key goal is the ability to switch between those capabilities, in real-time, while maintaining a small SWaP package. This capability will provide a significant technological advancement in the application of SAR systems that does not match any current programs under execution. The majority of current program customers are looking for incremental improvements for their already-defined mission space.

Summary of Accomplishments:
Year one focused on potential new CONOPS and the associated design tradeoffs required to build multi-mission payloads for those CONOPS. The first accomplishment was the development of MatLab-based models for the Synthetic Aperture Mobile Communications (SARCOM) CONOPS, which will add a high data rate communications link to our existing SAR hardware. The proposed communications waveform will mitigate the multipath fading channels found in this air-to-ground communications application. We also modeled an air-to-air link that will use the same waveform.

The second accomplishment was device characterization and antenna design. This was done to develop test sources and measurement techniques for the wide-band digitization capabilities of the planned SDSP hardware and software.

Significance:
This project will help Sandia continue to transition our existing surveillance and communications capabilities to the next generation of Military Unmanned Aerial Systems (UAS) platforms. This is critically important since UAS, and especially small UAS, may outnumber manned aerial platforms and other "national assets" in future military battle spaces. Those small UAS will also be more available to unit-level commanders and, hence, may provide more timely situational awareness than existing sensor platforms.

A Scalable Emulytics Platform for Observation of Windows-Centric Network Phenomena
151287

Year 1 of 3
Principal Investigator: C. T. Deccio

Project Purpose:
One challenge facing computer security researchers is the lack of tools for understanding large-scale emergent behavior of Internet applications. There has been some success scaling large arrays of Linux-based virtual machines (VMs) for the purpose of exploring the kinetics and mechanisms of such applications. Due to its large memory footprint however, Windows is at a considerable disadvantage. Since a large contingent of Internet hosts are running Windows operating systems (OSes), observing its behavior at the large scale that emulytics affords would be attractive. The goal of the research was to create ways to produce a scalable emulytics platform for Windows OSes where it will have more impact and value to cyber security.

The latest Windows OS, Windows 7, requires at a minimum 16 GB in disk storage and 1 GB of memory for a useable system. Our intention is to scale to 10^6 VMs, which will not be feasible without a drastic reduction in the required resources. Two approaches hold promise as a means to achieving this, which we will call low and high interaction emulation.

A low-interaction emulation involves using only the portions of the OS that are needed to execute the software that should lower the requirements. For high-interaction emulation we virtualize the entire OS, but only copy what changes from the baseline system. This means that the first instance of the OS is expensive but additional clones running on the same processor are much less expensive.

Summary of Accomplishments:
We have built a lightweight Windows 7 platform that runs in a kernel-based virtual machine (KVM) virtualization environment. Using a custom launcher we developed, we are able to boot up to 200 Windows VMs on a single host by overcommitting memory and compute resources. We use the kernel-shared memory (KSM) technology to share memory resources utilized by VMs on a single host with limited physical memory. Leveraging tools and methodology from the MegaTux project, we have an environment to deploy these VMs on lightweight Linux hosts comprising a cluster built for this purpose. In this contained environment, we have successfully launched a network of 65,000 Windows machines, each running an instance of an application. As part of our analysis, we collected some initial network-related metrics associated with the communication mechanisms of this software and wrote a report detailing our methodology and analysis.

Significance:
A high-fidelity Windows emulytics capability will enable new research into Internet-scale phenomena such as content distribution networks, any cast routing, and behavior of peer-to-peer applications; such a capability is important to cyber-security initiatives by several agencies.

Robust Classifiers for Dataset Shift Induced by Unmodeled Effects
153891

Year 1 of 2
Principal Investigator: H. Anderson

Project Purpose:
Classification accuracy is often limited by the fact that a signal of interest has been deformed from the ideal prototype signal by some unmodeled effect. For example, the observed signature of a target may differ from the expected signature due to dynamic, obscuring objects. Or, a scanning electron microscope (SEM) may produce images that degrade over time due to sensor drift so that image features of identical objects cannot be reliably compared. In traditional supervised learning, training signals are assumed to be representative of the observed signal. However, in the above scenarios, unmodeled atmospheric or sensor effects create a mismatch between training and observed signal's problem known as "dataset shift" in the machine learning community.

A typical approach to mitigate dataset shift is to restore the observed signal through blind deconvolution, etc., so that it may be reliably compared to the training signals. However, blind signal restoration is ill posed and may rely on assumptions that are violated in practice. Recently, we introduced joint deconvolution and classification (JDC) as a system-optimized alternative to mitigate dataset shift induced by a linear time-invariant system (LTI), and demonstrated convincing performance over traditional blind deconvolution-then-classification methods.

We propose a challenging generalization of JDC, in which classifiers are designed to be robust to a generally nonlinear, time-varying system, and utilize both ideal and non-ideal training signals. The proposed method will be applied to datasets that involves multiband imagery with complicated noise structures and challenging signal-to-noise ratio (SNR), which exhibits very low SNR, time-varying noise signatures, and where accuracy exceeding 99.99% is desired. In both cases, observed signals are corrupted by environmental and system effects that are difficult to model. Although we focus on these datasets, this work may benefit numerous existing and future applications.

Summary of Accomplishments:
During FY 2011, we developed algorithms for early classification of time-series data. The test sequences have been corrupted by unknown atmospheric attenuation, may have large sections with missing features, and exhibit warping in the time-axis (non-linear stretching/shrinking). To address these uncontrolled effects, we train algorithms using several examples of warped time-series data, and a single ideal time-series "sketch" or prototype of the ideal time-series. The algorithms learn the warping and corruption by comparing non-ideal training data to the ideal training sketch. Applied to target typing from multispectral time-series data, our algorithms outperform baseline supervised learning approaches.

A method for handling missing features in a support vector machine (SVM) classifier was presented in the IEEE Workshop on Statistical Signal Processing (SSP), "Expected Kernel for Missing Features in Support Vector Machines."

A second publication for early time-series classification with theoretical guarantees has been submitted to the IEEE Conference on Acoustics, Speech and Signal Processing (ICASSP).

Significance:
This research addresses the DOE mission to advance technologies to detect the proliferation of weapons of mass destruction, as well as the DHS objective to prevent technological surprise. If successful, the proposed research will greatly increase the ability to detect and classify objects in non-ideal environmental or sensor conditions.

Thin Magnetic Conductor Substrate for Placement-Immune, Electrically Small Antennas
154259

Year 1 of 2
Principal Investigator: T. W. Eubanks

Project Purpose:
An antenna is considered to be placement-immune when the antenna operates effectively regardless of where it is placed. By building antennas on magnetic conductor materials, the radiated fields will be positively reinforced in the desired radiation direction instead of being negatively affected by the environment. Although this idea has been discussed thoroughly in theoretical research, the difficulty in building thin magnetic conductor materials necessary for in-phase field reflections prevents this technology from becoming more widespread.

This project's purpose is to build and measure an electrically small antenna on a new type of non-metallic, thin magnetic conductor. This problem has not been previously addressed because non-metallic, thin magnetic conductor materials have not yet been discovered.

Summary of Accomplishments:
We successfully designed a thin (1% of a wavelength), non-metallic magnetic conductor substrate that reflects fields in-phase at its surface boundary at ultra-high frequencies of interest near the European industrial, scientific, and medical frequency band (433 MHz).

We fabricated and measured the resonant ceramic cylinders anticipated to make the substrate function properly. The ceramic cylinders have the dielectric constant (at 1 kHz) and the shape that we anticipated they would have after sintering them at over 1200 °C for several hours.

We designed and constructed a parallel-plate waveguide calibration kit to measure the reflection phase from our substrate and, through this measurement kit, we learned that our substrate was not working correctly due to the frequency dependence of the HF-402 ceramic's dielectric constant.

We demonstrated that the parallel-plate waveguide measurement system we created could not accurately measure the two-port S-parameters of high dielectric constant materials, so we will use a GR-900 coaxial cable system for future dielectric constant measurements.

Significance:
This research benefits intelligence, surveillance, and reconnaissance for the improvement of national security by enabling covert placement of antennas that can be attached to any surface without first inspecting the surface's material properties. The placement-immunity of these antennas will significantly improve their usability and reduce the amount of time needed to prepare them.

Simplifying Virtual Machine Security through Foundational Introspection Capabilities
154320

Year 1 of 2
Principal Investigator: B. Payne

Project Purpose:
Ensuring the security of a computer system requires the careful integration of many components. Key among these is security monitoring. Recent research trends show an increasing acceptance of external host-based monitoring techniques such as virtual machine introspection (VMI), a technique for viewing the runtime state of a virtual machine (VM). VMI's primary drawback, known as the semantic gap problem, is that it requires significant semantic knowledge and is error-prone due to its low-level nature.

Solving the semantic gap problem is hard because it requires encoding a complete understanding of the target system such that a monitoring program can readily access it. As a result of this overwhelming challenge, most VMI developers have created "one-off" solutions. This typically involves determining the information needed about the target system (e.g., through reverse engineering or program analysis) and then "hard-coding" it into a VMI-based program such that the monitoring functionality works in that program, but is difficult to use in other, related programs.

We propose to address this problem by providing a framework for integrating the "one-off" solutions into a database of semantic knowledge. Using this database, we propose to enable VMI-based programming at a higher semantic level that is less error prone. The key research components of this project include the following:

- A programming language and/or high-performance runtime that allows VMI-based application developers to access data and execute key algorithms from the target software using high-level symbolic semantics that are familiar to the developers
- A collection of program analysis techniques for extracting semantic information from software, vendor symbols, raw memory, and other key sources of information
- A runtime and/or compiler that provides automated handling of error conditions that are common in VMI programming, but uncommon in other settings, in order to simplify VMI-based application development
- Tight integration of each component described above with a VMI library

Summary of Accomplishments:
The project's primary accomplishments for FY 2011 include work on a virtual machine introspection library (LibVMI), and work on techniques to extract semantic information from software.

LibVMI is designed to provide low-level access to a running virtual machine's memory. This library is being developed with the goal of releasing the software as an open source project to foster community involvement and interaction. Below is a list of the LibVMI accomplishments in FY 2011:

- Design and implement a software patch to enable memory access of virtual machines running on the KVM virtualization platform
- Design a comprehensive memory introspection programmer's interface (API) to allow for reading and writing to a virtual machine's memory; also completed an internal peer review of this API
- Design software architecture for LibVMI library internals to enable virtual machine introspection across multiple virtualization platforms (currently Xen and KVM)

- Implement LibVMI API in the C programming language, and also provide a Python programming language wrapper to allow developers using LibVMI to work in either language
- Working to secure approval to release LibVMI as an open source project
- Created a public-facing web site for LibVMI (http://vmitools.sandia.gov)

Complementing LibVMI is a series of techniques for extracting semantic information from software. In particular, we focused on extracting the information needed to analyze memory from the kernel space of Windows and Linux systems in FY 2011. To achieve these goals, we developed the following tools:

- Tool to identify the Windows software version using only a physical memory view
- Tool to download debug symbols from a Microsoft server, and to parse these files to extract useful semantic information including type definitions
- Tool to perform static analysis of the C source code for the Linux kernel and extract type definitions and other semantic information.

Significance:

The successful completion of this work will help to push VMI into the mainstream. This foundational capability can then be leveraged to solve some of the most challenging computer security problems that we, as a community, face today. Some of the problems where VMI could play an integral role in the solution include secure operating systems, information provenance, malware detection and mitigation, fault-tolerant systems, provably secure systems, insider threat, forensics, and attack attribution. By developing better VMI capabilities at Sandia, we will be well positioned to participate in the solution to many of these key national security problems.

Leveraging Safety Applications for Global Revocation and Congestion Control in Vehicular ad hoc Networks
155408

Year 1 of 3
Principal Investigator: J. J. Haas

Project Purpose:
Wireless networking enables communication among highly mobile entities in many different arenas. Unmanned aerial vehicles (UAVs), soldiers, and ground vehicles form tactical or disaster relief mobile ad hoc networks (MANETs). Civilian vehicles will form vehicular ad hoc networks (VANETs) to improve vehicular safety. These two networks have widely different goals but have similar foundations in terms of security functionality; network participants should be authorized to use the network by a trusted authority, and participants that are deemed untrustworthy should have their authorization credentials revoked to limit the amount of damage they can do. In MANETs and VANETs, contact with trusted nodes may be limited due to funding constraints and the large areas these networks will cover.

A trusted authority (TA) will be unable to observe events that should lead participants' revocations. Thus, revocable offenses need to be detected in a distributed manner by the untrusted nodes. Such offenses should be reported to the TA opportunistically so that the TA can revoke the offenders' credentials and distribute information such that all nodes can identify the offenders. This process is referred to as global revocation (or attribution elsewhere) and is an open research problem, which we will address.

MANET or VANET conditions (e.g., density, wireless channel) vary widely due to nodes' mobility and, thus, require congestion control mechanisms to adapt. However, network congestion control mechanisms affect network connectivity and quality of service. We will investigate and design secure congestion control mechanisms that minimize, limit, or eliminate the influence attackers have on those mechanisms.

US Department of Transportation (USDOT) plans to mandate VANET capabilities in vehicles by 2013. Global revocation is a vital piece of VANET security systems, without which VANET systems will not have a means of feedback to remove revocable entities. Congestion control may be necessary for increased safety application effectiveness. Attacks on insecure congestion control algorithms may reduce safety application effectiveness.

Summary of Accomplishments:
With regard to our work on network congestion control, we have run approximately 81,000 simulations (and counting), working towards providing the motivation for congestion control in vehicular ad hoc networks (VANETs). To enable a greater realism in the simulations, we have implemented a new channel model that is based on ray tracing, which was presented at the VANET 2010 workshop. To reduce the execution time our simulations require, we have profiled and optimized my simulator's performance, including adding multithreading (parallelization). We have additionally refined our analysis tools to provide a more fine-grained interpretation of the results of the simulations. This refining should provide more meaningful insight and result in more direct conclusions.

We have defined an attacker model for our work with global revocation. We have assembled a mathematical characterization of the attack surface for the intersection collision warning (ICW) safety application, as we had implemented the ICW in previous work. Using this model, we built a Monte

Carlo simulation tool and used it to determine that the attack surface was not the empty set and would not be completely protected under a detection mechanism that we developed. As a result, we have a suggestion for modifying the ICW safety application such that this protection is effective. To evaluate this new approach or rule set, we have built a tool to determine what resources an attacker needs to successfully attack vehicles under the old rule set. These results indicated that an attacker likely could use a single standard radio to successfully attack at least 50% of vehicles in the neighborhood of the attacker's radio, and using two radios increases his probability of successfully attacking vehicles to 90%. Additionally, we have enumerated sources of error and uncertainties that could affect the updated ICW safety application, and questions that arise as a result.

Significance:
VANETs may become one of the largest deployed wireless networks. As of 2008, there were 256 million vehicles on the road in the United States. VANET safety applications are one of the main modes of communication for achieving the goals USDOT has laid out in their IntelliDrive program for improving road safety. Additionally, DHS has identified transportation as one of their critical infrastructure key resources (CIKR).

Global revocation mechanisms will provide a missing piece in the security framework for VANETs, and are directly applicable to DoD autonomous ground vehicle, sensor systems, and MANETs. Without the ability for the certificate authority (CA – the central authority or authorities that authorize vehicles to use the network) to conclusively or reliably remove malicious actors from a VANET, there will be no feedback mechanism to limit the amount of damage an attacker can achieve, that is, the number of vehicles the attacker can affect may not be limited. One way that we have approached this problem is to make use of the physics involved in this problem, which is an approach that we believe may be easily extended to other cyber physical systems. It includes process control systems and smart grid. Inherently, the problem that global revocation is trying to address is that of the insider threat, which has been identified as a major threat to cyber security.

Secure congestion control algorithms can be used to alleviate VANET congestion, increasing safety application effectiveness and reducing attacker influence or control. The attack on congestion control mechanisms that should be mitigated is the following: an attacker may generate false or erroneous packets that indicate the network is in a state other than what it actually is, and thus, the attacker may be able to tune the congestion control mechanisms on board other vehicles to his liking. One of the fundamental problems to congestion control is how can a system gather information from its environment (e.g., other vehicles) and not allow other actors who are a part of that environment to control or to limit that control of critical systems (e.g., congestion control mechanisms). Specific to congestion control for VANETs, an attacker who can get another vehicle to turn down the rate at which that vehicle is broadcasting or the transmission power that vehicle is using may be able to reduce the effectiveness of safety applications.

Hybrid Optics for Broadband Optical Systems
155554

Year 1 of 3
Principal Investigator: J. Choi

Project Purpose:
Space-based optical payloads are designed and fabricated to perform in harsh thermal and radiation environments. These unique environments limit the choice of optical materials, as they need to be radiation resistant, withstand mechanical forces of launch, and have broad spectral transmission. The limited number of radiation resistant optical materials removes degrees of freedom to correct chromatic aberration. Chromatic aberration refers to different colors of light focusing at different positions, resulting in broadband systems to appear out of focus except at one wavelength. The effect is caused by the material separating different colors of light in different angles, called dispersion. Using more than one glass material enables multiple colors to be brought into focus at the same position. However, with the small number of available materials, the optical engineer is often forced to add more lenses to the optical design to achieve a high performing system. The result is that space-based optical systems tend to be heavy, more sensitive to alignment errors and complex with many optical and mechanical elements.

Diffractive optical element (DOE) is a fine periodic structure that causes dispersion of light, the degree of which can be tailored by the design of the periodic structure, independent of the material properties. Hybrid lenses, lenses with a DOE patterned into one of the surfaces, are starting to find their way into various systems. Due to efficiency and manufacturing challenges, use of these elements has generally been restricted to longer wavelength and narrow bandwidth systems. Current state-of-the-art hybrid lenses do not meet the performance demands of space-based remote sensing systems, where high efficiency and broadband operation are important. An innovative solution to expand the working bandwidth of DOEs would push the design trade space beyond what is currently possible as hybrid systems have the potential to require fewer materials, reduce size and weight, and reduce mechanical and alignment tolerances.

Summary of Accomplishments:
We evaluated available diffractive fabrication methods and identified lithographically fabricated multilevel binary diffractive lens to be the best approach for integration into an imaging system with a moderate aperture size in the visible spectrum. We designed two imaging systems of comparable optical performance – one with a DOE to correct chromatic aberration and the other using traditional refractive achromats – and studied parameters of the hybrid imaging system.

We used the two designs to illustrate how diffractive elements impact system size, weight, and the number of required refractive elements. The traditional optical system required two materials to correct chromatic aberration of the system, while our design of the hybrid optical system required only one refractive material correcting chromatic aberrations with only a single more commonly utilized optical material. Although both systems had comparable volume, the hybrid system had reduced weight by using one fewer refractive element. Tolerance analysis performed for the two systems revealed that the hybrid imaging system has looser tolerances for both fabrication of lenses and alignment of the optics. All of the custom components for the narrowband hybrid system including the DOE, lenses, and the housing were fabricated and received.

Significance:

The proposed research and development effort has the potential to reduce size, weight, and complexity of broadband optical systems, addressing the continual need for such improved systems in space, military, and intelligence communities.

Identifying Dynamic Patterns in Network Traffic to Predict and Mitigate Cyber Attacks
155799

Year 1 of 3
Principal Investigator: J. D. Wendt

Project Purpose:
The purpose of this project is to improve Sandia's cyber defenses against social engineering attacks. We believe that for attackers to craft personalized phishing (spear phishing) attacks, web-based research — including research via our web sites — will likely occur to identify appropriate targets. In this project, we work to visualize visit patterns to our web pages.

This research leverages Sandia's robust research environment with three researchers from three disparate organizations. Furthermore, we are making contacts and sharing information with other lab-directed research and development projects, as well as leveraging tools created for collaborative work.

Summary of Accomplishments:
We have developed tools to collect and store the data necessary for our analysis as well as some early results that provide new ways for analysts to look at the web server logs. We expect these visualizations to help analysts quickly identify correlations between different visitors' visit patterns.

Significance:
Successful attacks against Sandia jeopardize our intellectual property and the integrity of our computing infrastructures. As spear phishing has shown itself quite effective at introducing malicious software past conventional cyber security systems, we are working to innovate new defenses against these tactics.

Alternative Waveforms for New Capabilities in Radar Systems
155802

Year 1 of 3
Principal Investigator: R. M. Naething

Project Purpose:
Synthetic aperture radar (SAR) imaging systems achieve high resolution in range by transmitting very high bandwidth waveforms. The radar's high bandwidth channel can also be used to transmit and receive information at very high data rates. Simultaneous data transmission and radar imaging can also be achieved by modulating the radar's waveform with information at high data rates. Embedding a communication link into the radar sensor while simultaneously imaging enhances existing sensor capacities and enables new missions. However, the radar waveform is no longer predictable and the information content modulated into the waveform can have undesired effects on the resulting radar image.

The principal goal of this work is to research and develop new waveforms that extend the capabilities of current imaging radar systems to include simultaneous communications and other applications that are enabled with radar communications.

We examined waveforms that provide the ability to embed information into the transmitted waveform to perform simultaneous communication and imaging. We investigated and developed new radar waveforms that are optimized for radar image performance while maximizing channel capacity. We also examined the use of alternative waveforms to mitigate susceptibility to interference, both from intentional jamming and the simultaneous operation of other communication and radio frequency (RF) imaging devices. We examined waveforms that allow multiple radars and suitably designed communication systems to operate concurrently in the same RF spectrum. Finally, we also researched waveforms that do not indicate that the radar channel is being used for communications.

While current methods provide several bits-per-coherent processing intervals or even bits-per-pulse, the ability to perform high quality imaging while also transmitting at maximum channel capacity with a low observable waveform is difficult. However, dual use of limited RF spectrum will become more valuable as contention for spectrum increases.

Summary of Accomplishments:
We examined a wide variety of potential waveforms and their potential application for simultaneous communication and SAR imaging. Several promising families of waveforms have been identified and we have begun characterizing these in depth. These include multicarrier phase-coded (MCPC), pseudo-random waveforms, and code division multiple access (CDMA) signal families. We determined that range-Doppler behavior (the ambiguity function) is not a sufficient criterion to measure imaging performance.

Initial work has focused on MCPC signals. MCPC signals are a family of signals that utilize orthogonal frequency division multiplexing and have properties that can simplify the problem of segmenting a portion of the transmitted waveform for data. They provide the ability to pick a discrete sub-segment of the transmitted waveform to dedicate to imaging, communication, or both. This would allow the end user with the capability to determine what level of imaging performance and data throughput is required and the ability to tailor the transmitted waveform to those specific requirements. For MCPC signals, the sequences used to modulate the orthogonal carriers must be picked to simultaneously optimize the peak-to-mean envelope power ratio (PMEPR) and ambiguity function. Blindly choosing modulation sequences results in a transmitted signal with little transmitted power and poor imaging performance. Existing MCPC implementations use sequence families to modulate the orthogonal carriers that are not suited to carrying data, and the choice and optimization of these carrier sequences is still an open problem. We have begun examining how these carrier sequences can be picked to carry data while still yielding good imaging performance (as measured ambiguity function and the PMEPR).

In the coming year, we will continue examining the problem of choosing optimal signals and signal parameters as well as suitable criteria to fully characterize the signals and allow comparison of imaging and communication performance between disparage signal families.

Significance:
Any application of real time acquisition of SAR data would benefit from simultaneous imaging and communication. SAR systems have applications in nuclear nonproliferation (DOE), border monitoring (DHS), and various defense (DoD) missions.

Improving Shallow Tunnel Detection from Surface Seismic Methods
156137

Year 1 of 3
Principal Investigator: N. Bonal

Project Purpose:
The purpose of this project is to understand the effects tunnel construction has on seismic waves and to improve detection and location of clandestine tunnels and/or facilities using seismic methods. Seismic reflection and refraction have been viewed as some of the better methods to detect tunnels, but results have been good in some cases but not in others. A recent study of competent rock shows that the largest responses from the tunnel are not reflections or refractions. Therefore, these methods may not be as useful for tunnel detection as previously thought. Additionally, the damaged zone (e.g., fractures created/enlarged by tunnel construction) has a negligible effect on reflected and refracted seismic waves. However, clandestine tunnels in the near surface are often constructed in weak rock and below the water table, where pore spaces around the tunnel become dewatered. These effects may have a significant impact on seismic waves and should be investigated. Also, signal-processing techniques other than seismic reflection and refraction should be developed for tunnel detection. The goals of this project are to: 1) determine the effects, if any, changes in rock properties of the tunnel "halo" due to construction (e.g., material fracturing and pore dewatering) in the near surface have on seismic waves and 2) increase tunnel detection ability by improving signal processing techniques including reverse time migration (RTM) and surface wave diffraction. This project aims to accurately model the area around the tunnel, the halo, which has been created by the tunnel's construction. Previous studies do not address the effects of dewatering or construction in weak, poorly consolidated materials, which may be significant. Modeling seismic wave propagation through tunnel halos will demonstrate if halos have a significant effect on seismic velocities. The proposed work will utilize preexisting data from near surface clandestine tunnels to compare modeling results and test processing techniques.

Summary of Accomplishments:
We have made significant progress on designing a wavefield transformation technique that searches for seismic diffractions off subsurface voids. The diffractions of body waves and surface waves form a distinct arrival on multichannel, active-source records. These arrivals come at times that differentiate themselves from direct arrivals, refractions, and reflections. Two MatLab algorithms (one for surface waves and one for body waves) have been prototyped that transform the seismic wavefield from distance-time (x-t) space to diffraction slowness-depth (p-d) space. In the transformed p-d wavespace, tunnels should stand out as high amplitude bulls-eyes near the proper slowness and depth coordinate. This technique is similar to beamforming, but with curved diffraction forming the beam, instead of plane arrivals. These algorithms are currently being tested on synthetic seismic waveforms that model the ground and tunnel characteristics of the Moffatt railroad tunnel in Colorado.

We have also made progress with the RTM code. Seismic traces from the sources are now normalized to minimize the effects of source-earth coupling that may be different at different source locations. In addition, the recorded data contains frequencies above the maximum frequency used to determine the grid spacing used in the model for back propagating the field data. Therefore, the data are now low-passed filtered prior to the time-reversal process. This filtering removed some of the grid dispersion effects detected in images produced by prior attempts using unfiltered data. The images from filtered data were sharper. Future work on improving this code includes investigating the time-dependent boundary condition implementation for the RTM process. The effects of surface waves contaminate the final image and makes detection of very shallow targets problematic. It is believed that treating the vertical particle motions as a time-dependent boundary condition will eliminate surface waves in the time-reversed wavefields.

The waveform diffraction processing technique can be used to increase the signal-to-noise ratio of data containing near surface tunnels. Additionally, the RTM processing technique improvements which reduce artifacts in the data should be used as a standard procedure. Both of these techniques increase the potential to detect and locate tunnels and potentially other seismic wave scatterers (e.g., facilities, buried objects). Therefore, these techniques should also be of interest to signal processors.

Significance:
This work is broadly applicable to multiple DOE mission areas. The ability to detect and characterize underground facilities has application to the DOE nonproliferation mission and to Defense Advanced Research Projects Agency (DARPA), Defense Threat Reduction Agency (DTRA), and other DoD customers. Additionally, DHS and other federal agencies can apply this work to domestic and foreign border security through improved detection of border tunnels.

Dynamics of Point Source Signal Detection on Infrared Focal Plane Arrays
156138

Year 1 of 3
Principal Investigator: G. Soehnel

Project Purpose:
We will develop a model that describes the effects of charge diffusion and optical blooming on the point source response of infrared (IR) focal plane arrays (FPAs). Sandia leads development and deployment of state-of-the-art mercury cadmium telluride (HgCdTe) FPAs for IR optical systems. These sensors are highly desirable for remote monitoring systems. Two desirable detection scenarios include: 1) detection of small dim targets in slowly changing scenes and 2) the detection of highly temporal, bright, point sources. Optical measurements on current systems indicate modulation transfer functions (MTFs) are incorrect due to unknown effects at the FPA pixel level. Studies observing these phenomena produced by bright point sources on visible (Silicon) FPAs are under way. The effects on IR FPAs are more severe but also less understood theoretically and much more difficult to characterize experimentally.

We will, for the first time, generate sub-pixel stimulus and develop models to describe the optical and electrical blooming occurring within the IR photodiodes and arrays as a function of spot intensity, wavelength, position, boundaries, and motion. A complete understanding of any unknown detector or read-out based anomalies will be gained by the following experimental scenarios: 1) a single sub-pixel spot, 2) dual spots resembling closely spaced objects, and 3) a bright spot with a controllable background. Measuring the response of a sub-pixel spot on an optical system and/or a detector is a notoriously difficult problem. To achieve our objectives, we will leverage recently acquired test hardware and test methodology developed for visible FPAs. The longer wavelengths, liquid nitrogen operating temperature, and the additional layers and materials present in the IR FPAs will present additional challenges. The results, however, will increase our understanding of IR FPAs and provide advanced knowledge for improved operational performance for space based and terrestrial applications.

Summary of Accomplishments:
We have assembled and analyzed the hardware and optics for the spot-scanning experiment. We designed experiments that validated the spot size and profile is similar to the design specifications. We also wrote the programs necessary to perform spot scans that coordinate moving the motorized stages and operating the FPA. During this time we discovered that, under an appropriate configuration, the FPA can be operated at room temperature and pressure. We were able to get reasonable responses under the spot illumination, which allowed us to develop a scanning program and post processing algorithms without the need to cool the FPA. We were able to perform warm scans that produced adequate data to generate MTF curves. While working on the experimental setup, we also selected an approach for modeling the point-source response. We implemented a Monte Carlo simulation in MatLab in which it randomly generates photo-carriers and tracks them through a random walk until they are collected. This approach is appealing because there are no constraints on the device geometry, and it is a 3D simulation. Initial results from the simulation have compared well to a Blouke-Robinson model approach. We are starting to go cold with an FPA in the Dewar. A full week of testing on a target FPA has been completed. These initial results show that the 4 pixels scanned produce point-spread functions (PSF) and MTF curves that are very consistent. Also, the lab data is agreeing very closely with the Monte Carlo simulation.

The spot-scanning experimental station is now complete and able to perform scans on the FPAs. To our knowledge, this is the only lab experiment capable of performing IR spot scans on FPAs of this kind.

The ability in itself to project a sub-pixel-sized spot onto an FPA inside a liquid nitrogen cooled Dewar is of great interest. This ability is beginning to generate interest for various testing of things other than point-source response scanning such as ghosting effects. The PSFs generated by the spot scans will help us better understand the blurring that occurs due to the detector. The end result will be a better model of the FPA to incorporate into processing of data that comes in from the field. The FPA's contribution to the system PSF (and modulation transfer function, MTF) is of particular importance because point source detection is a key application of the FPAs.

Significance:
Lab data in competition with further work on the Monte Carlo simulation will help us better understand the physics of charge generation and collection within the FPA. We hope to better understand how the pixel geometry, wavelength, and temperature affect the width of the PSF. This will not only impact our ability to interpret data from our FPAs, but will also provide insights into what things about the FPA design itself affect performance the most. These improvements for space-based and terrestrial sensor systems will have enormous impact on national security.

Optical Refrigeration in Semiconductors for Next-Generation Cryocooling
157310

Year 1 of 3
Principal Investigator: D. A. Bender

Project Purpose:
Current refrigeration technology for cooling space-based infrared (IR) focal plane arrays and sensors uses mechanical cryocoolers reaching temperatures down to approximately 75-120 K. Such systems contain moving parts, which in time can wear out and contain refrigerants that can leak. These properties limit reliability and operational lifetime. Mechanical coolers produce vibrations that can lead to blurring during image acquisition. A balanced assembly minimizes vibrations, but does so at the expense of increased payload mass.

The aim of this research is to investigate challenges in optical refrigeration (or laser cooling) of semiconductors by: 1) leveraging Sandia's capabilities to grow unique highly doped GaAs/InGaP double heterostructures and 2) by partnering with the University of New Mexico (UNM) to spatially resolve the temperature profile of a sample under test in a cooling experiment. Optical refrigeration in semiconductors can potentially provide reliable, vibration-free, low-mass cooling of detectors and optics to <20K, representing a significant benefit for remote sensing applications.

Laser illumination has achieved cooling of dilute gases of atoms or ions resulting in substantial scientific progress. Within the last 15 years, optical refrigeration of solid-state systems has advanced rapidly from a slight 0.3 °C temperature change, to achieving cryogenic temperatures with 150 °C of cooling. Optical refrigeration in solids was first demonstrated in 1995 using a rare-earth doped glass. Further refinement of techniques and materials research allowed cryogenic temperatures of 155 K to be achieved in ytterbium-doped LiYF4 crystals. The postulated minimum achievable temperature for LiYF4 is limited to 100K. In contrast, direct band-gap semiconductors are predicted to achieve much lower temperatures with greater cooling power densities because the constituent atoms of the host material participate in cooling rather than a small percentage of dopant atoms. However, net cooling of a semiconductor has not been realized. We want to investigate possible routes to achieve this unrealized goal.

Summary of Accomplishments:
To date, the optical refrigeration project has successfully modeled luminescence extraction from semiconductor double heterostructures excited by an optical source. We have found that the extraction efficiency can range from 17% to 27% for readily available optical materials such as ZnS and ZnSe and semiconductor GaAs thin films of 750 nm thickness. The modeling included a variety of geometries based on a hemispherical lens, a slab, and a prism. Additionally, we have grown GaAs/GaInP double heterostructure as candidate laser coolers. The lifetimes of our first generation samples were measured with our collaborative partner, UNM, to be 2.53 to 7.26 microseconds. The modeled extraction efficiency coupled with the measured lifetimes represents adequate conditions for achieving laser cooling. The results from this fiscal year have resulted in submission to the Photonics West - Laser Refrigeration in Solids Conference.

The expected outcome of this project will result in a new optimized semiconductor double heterostructure with long nonradiative lifetimes based on systematic study of the doping density in the passivation layers. With this structure we will demonstrate, for the first time, laser cooling in a semiconductor platform. We will be able to prioritize some of the mechanisms that have prevented laser cooling in semiconductors thus far.

As yet optical refrigeration in semiconductors has not been demonstrated; however, the accomplishments of our project coupled with modeling results from the literature suggest we should be able to achieve cooling. We are poised to make these measurements in the upcoming year. If background absorption in the semiconductor material is low enough, we should achieve net cooling in semiconductors for the first time. We expect an initial demonstration of optical refrigeration in semiconductors will serve as a catalyst for rapid future high visibility development.

Significance:

Optical refrigeration has potential deep impact for cooling optics and focal plane arrays used in remote sensing activities. Compared to conventional cryocooler technology, optical refrigeration has higher reliability, an absence of cryogenic fluids, solid-state and vibration-free operation, long operational lifetimes, compactness, and low mass. Competing solid-state technologies (i.e., Peltier coolers) cannot reach temperatures below 170K, while the minimum achievable temperature for optical refrigeration in semiconductors is predicted to be 20K. A demonstration of optical refrigeration in semiconductors could be an important first step in realizing a new technology of solid-state cryogenic cooling.

Silicon Photonics for Ultra-Linear RF Photonic Devices and Links
157633

Year 1 of 3
Principal Investigator: C. Derose

Project Purpose:
The purpose of this project is to discover and demonstrate silicon photonic devices and subsystems that will enable efficient analog optical communications. Analog electrical radio frequency communication links suffer from susceptibility to electromagnetic interference (EMI), propagation losses which increase with the square root of frequency, and the large weight of copper lines. One way to overcome these disadvantages is with analog radio frequency photonic links (RF photonic links). RF photonic devices offer significant size, weight, and power (SWaP) advantages over traditional microwave components; moreover, RF signals transmitted on an optical carrier are immune to noise from EMI. Traditionally, external electro-optic lithium niobate modulators have been used for electrical-to-optical signal conversion; however, they suffer from a limited spurious free dynamic range (SFDR) and incompatibility with direct integration of optical photo detectors and complementary metal-oxide-semiconductor (CMOS) electronics.

Silicon is at the forefront of low power digital optical communications research. However, to date, little attention has been given to silicon for analog optical applications. Silicon offers the potential to create ultra-linear RF photonic devices in a process that is compatible with rad-hard CMOS electronics, and integrated germanium (Ge) photodiodes, a capability that no current RF photonic technology offers. Digital silicon photonic modulators have been demonstrated with power consumption as low as 3 fJ/bit, with an area of only a few um2; therefore, it is predicted that RF silicon photonic devices will enable a significant decrease in SWaP for RF. RF silicon photonics has the potential to increase system bandwidth by an order of magnitude or more, linearity by nearly two orders of magnitude, and significantly reduce susceptibility to electromagnetic interference.

Summary of Accomplishments:
A new method for characterizing the optical loss of waveguides was developed. Furthermore, we have developed an in-house optical mode solving solution that will be integrated with semiconductor device simulators next fiscal year. This will give Sandia a unique capability for optical simulation coupled with semiconductor device physics.

Significance:
A complete RF silicon photonics platform that is CMOS-compatible represents a new capability that will have significant benefits across nearly all DOE and DoD mission areas. A complete RF-silicon photonics platform will have wide-ranging impact. Importantly, the completion of this platform will be possible only through a rigorous study of the device parameters, as stated in this research effort.

Integrated Auto-Catalytic Composite Strategies
158518

Year 1 of 3
Principal Investigator: J. Carroll

Project Purpose:
Polymeric composites that autonomously respond to external stimuli provide a wealth of novel engineered solutions (e.g., self-healing polymers for structural and aeronautical applications). In this mechanical embodiment, micro-encapsulation techniques enable compartmentalization of reactive components (i.e., resins and curing agents). When the matrix is subject to structural damage, the capsules rupture and polymerize within the crack; thus, restoring mechanical integrity (i.e., self-healing). However, to date, no one has identified a methodology for an electrical analog that results in high quality radio frequency (RF) conductive traces. It is the intent of this research to demonstrate the feasibility of polymeric composites that respond to external stimuli by autonomously initiating an electroless metallization reaction – resulting in conductive traces for enhanced application functionality.

"Electroless plating" is a time-tested, room temperature chemical reduction process wherein a metallization reaction proceeds spontaneously on select surfaces. This plating process provides a means to produce uniform coatings on a wide array of substrates for mechanical and electrical applications. The versatility and cost effectiveness of this process has resulted in widespread use throughout the industrial sector, but the underlying process is overly limited. The reduction reaction only initiates when a substrate is physically submerged into a solution bath containing the reducing agent. Through compartmentalization and embedding of plating reactants in a flexible composite, a new creative and innovative sensor technology will be realized (via an autonomous response mechanism). Thus, the initial insulating reactants proceed to form conductive traces upon rupturing within the polymer matrix.

Summary of Accomplishments:
We have demonstrated initial prototypes highlighting the methods and capabilities to microencapsulate charge salt species. Current efforts have identified a room temperature copper electroless deposition formulation and near term activities are addressing the requirement for micro-encapsulation. 2D electroless chemistries have been demonstrated.

Significance:
Due to flexible form factors and integration methodologies, the proposed composite offers new advantages to tagging, tracking, and locating systems (e.g. new routes to novel biological, radiological, and chemical sensors). Specifically, DOE for nuclear non-proliferation, DoD for new sensor/detection capabilities, and DHS for product, facility, and infrastructure monitoring of high-priority assets will benefit from the new form factor and sensing capabilities that this work offers.

A High-Voltage, High-Current Thyristor Stack Command Triggered by dV/dt — An Improved MOS-Controlled Thyristor-Like Nanosecond Closing Switch
158698

Year 1 of 3
Principal Investigator: R. J. Focia

Project Purpose:
The metal oxide semiconductor (MOS) controlled thyristor (MCT) currently used as the closing switch in solid-state firesets has exhibited failures on the bench and in the field during pre-shot safety checks. The cause for the failures is unknown and manufacturer support on the failure issues has been limited at best. The MCT consists of thousands of cells switched in parallel and is currently available from only a single source. Although the MCT has higher time rate of change of current (di/dt) capability than ordinary thyristors, switching thousands of devices in parallel can be problematic and a single source supply of devices could be detrimental to the long-term success of a product. The challenge in this effort will be to fabricate a hybrid solid-state closing switch with voltage hold-off and current handling capabilities equal to or better than that of the MCT, but with a higher di/dt capability and improved reliability. Proof-of-concept of the new three-terminal solid-state closing switch will be accomplished by fabricating the hybrid switch by monolithic integration of commercially available thyristor and diode chips, metal-oxide-semiconductor field-effect transistor (MOSFET) switches, and a minimum number of passive components.

The potential outcome of this research and development effort is a new, command trigger-able high power solid-state closing switch for use in pulsed-power applications. We intend to creatively exploit a known effect in thyristor structures in order to provide a solid-state closing switch capable of high hold-off voltages, nanosecond or faster closing times, low-jitter, and carrying high pulsed currents. Although proof-of-concept will be demonstrated using a monolithically integrated device, we also designed, modeled, and conceptualized a fabrication process for an entirely new multi-junction thyristor-like structure. The new closing switch will have wide application in the pulsed power community.

Summary of Accomplishments:
Equipment in our lab was surveyed to determine deficiencies in supporting experiments for this project. Items deemed necessary to support experiments but not available in our lab, were selected and procured. In the proposal for this project, only silicon thyristors were planned for use in prototyping. Devices made from other materials such as gallium nitride (GaN) and silicon carbide (SiC) were to be considered for future use to exploit desired properties of these wide bandgap materials. At the time the proposal was written, it was not known if thyristor structures were available in these other materials. Initial research uncovered one company (GeneSiC Semiconductor) that fabricates SiC thyristor structures that should be suitable for use in prototyping experiments. We have established a nondisclosure agreement (NDA) with this company and are currently in discussions with them in order to learn more about their SiC thyristor structures and obtain device chips for use in experiments. Preliminary plans were developed for fabrication of a Phase I prototype, involving the stacking a diode and multiple thyristor chips and encapsulating them into a low inductance, command triggerable switch package equivalent in size to a commercially available MOSFET.

We have procured several different packaged thyristor types which will be subjected to dV/dt testing. A test fixture has been designed to accommodate testing of the various thyristor types.

Significance:
The potential impact of this R&D effort is that it results in a new high-voltage, high-current solid-state closing switch that outperforms, and is more reliable than, the MCT currently in use in firesets at Sandia and elsewhere. Improved performance and reliability in firesets is directly tied to the national security missions of DOE and possibly other federal agencies. If we fabricate and use optimized thyristor structures in our hybrid switch, the potential exists for a new subnanosecond solid-state closing switch from which the entire pulsed power community would benefit.

Explosives Detection with Neutrons from a Short-Pulse High-Intensity Neutron Source
158700

Year 1 of 3
Principal Investigator: O. Doron

Project Purpose:
This project is investigating the use of a short-pulse high-intensity neutron (SPIN) interrogation source coupled with neutron and gamma ray sensors to find buried explosives. The approach promises a powerful new method to locate buried explosives (i.e., landmines and unexploded ordinance) deeper in the ground, faster, and more accurately than is possible with current methods. The current searching depth and time to find objects with active neutron interrogation technologies is relatively shallow due to two limiting factors: the intensity and duration of the neutron pulse from a neutron generator (NG) and the poor signal-to-noise ratios (SNR). Traditionally, finding explosives in a large area requires many neutrons and a high SNR. However, it is difficult to achieve both of these requirements because as the production rate from an NG increases the SNR decreases.

Preliminary data for SPIN interrogation of fissile material shows that this may provide capabilities that require two orders of magnitude less neutrons and 100 times shorter sample time than state-of-the-art systems, including the associated particle technique (APT). The NG used for this work has a pulse width in the 10-nanosecond range vice the microsecond range, which is standard for NGs. The narrow width of the pulse in the NG can be taken advantage of in several different ways, including the increase of SNR, and with technology advancements and narrower pulse widths, time of flight (TOF) measurements will be possible as well. Currently an APT NG can provide sub-nanosecond TOF timing resolution. The neutron and gamma ray detectors are highly sensitive and selective of either neutron or gamma rays. The combination of the NG and detectors used in the system will also increase the sampling depth and the probability of locating explosives.

Summary of Accomplishments:
Analytical models have been developed and nominally verified with computer models. The models demonstrate the ability of the proposed system to reduce collection times over the current state-of-the-art by roughly three orders of magnitude at shallow depths to just over two orders of magnitude at depths approaching 90 cm.

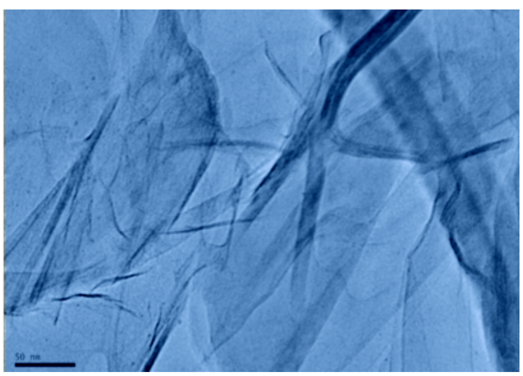
Significance:
Explosives detection is one of the common requirements of the DOE/NNSA/DoD/Sandia national security missions. Also, tunnel detection is important to the DHS mission of border security. The projected improvements that this project could bring to the areas of explosive and tunnel detection would benefit the national security missions of all of the agencies mentioned above. Explosives detection is also important for unexploded ordinance disposal, which is a high-priority environmental concern.

ENERGY, CLIMATEǐ AND IN&2 !3425#452% SECURITY INVESTMENT AREA

Projects in this investment area focus in one of three objectives, namely: to accelerate the development of transformative energy solutions that will enhance the nation’s security and economic prosperity, to understand and prepare the nation for the national security implications of climate change, and to develop and apply analytical approaches to secure the nation’s critical energy infrastructure against natural or malicious disruption.

Membranes and Surfaces Nanoengineered for Pathogen Capture and Destruction
Project 130749

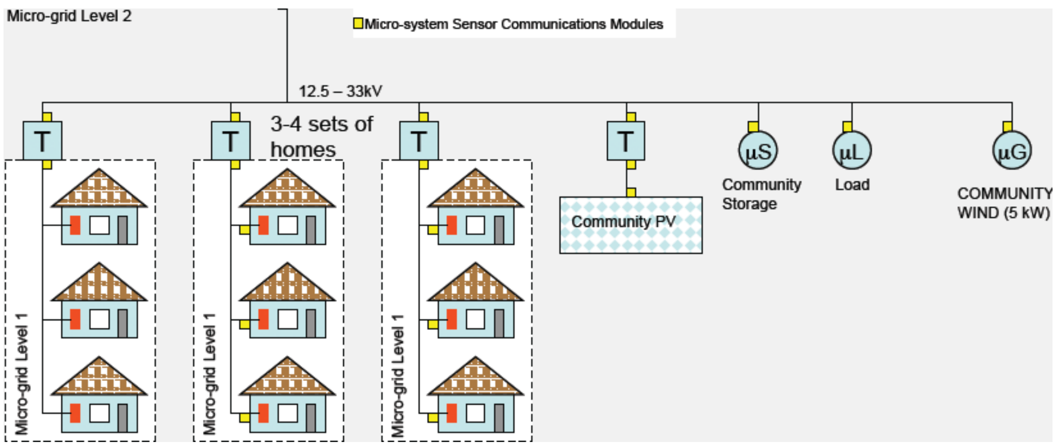
This project has developed advanced multifunctional coatings for water filtration media (such as reverse osmosis membranes). These coatings both trap microorganisms chemically rather than physically; and self-clean by using light to trigger decomposition of trapped. This ensures that very small pathogens such as viruses are trapped and destroyed, and that fouling of membranes by bacterial growth—a pervasive problem— does not occur. We live in an era when half the world does not have reliable source of clean drinking water, and therefore, the generation of potable drinking water from contaminated water is a crucial global issue. Hence it is critical that water purification membranes function reliably and efficiently. This is particularly true given the intimate connection between water and energy.



Colorized micrograph of delaminated titanate coating for water filtration membranes and other media

Scalable Microgrid for a Safe, Secure, Efficient, and Cost-Effective Electric Power Infrastructure
Project 130752

This project is researching a fundamental shift in the way our society manages electricity transmission. This is necessary because our current power grid is one-dimensional; power generated by burning fossil fuels and delivered to customer loads (electricity consuming devices). This grid cannot handle a significant penetration of renewable-energy generation (wind and solar) because of fluctuations in the supply of electricity from changing weather conditions, bidirectional power transport in a distributed network (customers with solar photovoltaic panels, for example, returning excess electricity *into* the grid), and also, safety and security issues associated with working on a grid with numerous power sources. Hence, the solution offered in this project is to arrange the network as a series of locally controlled intelligent microgrids, each of which is scalable at multiple levels (e.g., homes/businesses, neighborhoods, cities, and regions). This new power grid architecture uses information networks to enable real-time cooperative generation, intelligent metering, and load management functions to provide decentralized coordination of potentially millions of distributed generation sources and loads in an active, adaptive virtual "super-grid" that is stable, secure and sustainable.



The concept of a scalable microgrid

Energy, Climate, and Infrastructure Security Investment Area

An Ion Beam Platform for Screening and Studying Materials for Use in Fast Neutron Environments
130744

Year 3 of 3
Principal Investigator: K. M. Hattar

Project Purpose:
Our country's energy needs are driving a renewed interest in nuclear power generation and waste management by reviving fast neutron reactor technology. Fast neutron reactors will drive materials requirements in different directions from the more standard thermal neutron reactors. In order to support missions such as fuel cycle research and development (FCR&D) and generation IV nuclear energy systems, we must find a way to measure, understand, and predict materials properties at high temperatures and under high energy irradiation. However, there are presently no operating fast neutron reactors in the United States.

To address the lack of fast neutron availability for fuel cladding materials development and screening, we are researching the use of high-energy (MeV) ion irradiation combined with a suite of novel, microscale techniques to characterize the thermomechanical behavior of advanced cladding materials as a function of stress, temperature, and irradiation damage level. While ion beams have been used to simulate neutron damage for quite some time, there has been an inability to measure mechanical properties in the extremely small damage volumes produced by heavy ion beams. These mechanical properties will be determined by expanding the extant in situ capabilities of the ion beamline to include high temperature and mechanical testing capabilities. In particular, we are developing microscale tests based on the recent work in focused ion beam produced micropillars. We are also determining the ion-fast neutron damage equivalence for fuel cladding steels through ion irradiation experiments, ion cascade simulations, and molecular dynamics simulations.

This project provides methods for discovering the fundamental science behind irradiation damage and mechanical behavior in metallic alloys that will be vital to the nuclear fuels modeling efforts at Sandia. This ion beam approach will also provide a screening capability for studying the irradiation damage and effects in new alloys.

Summary of Accomplishments:
We produced two sets of diffusion couples — one of 316L and various refractory alloys and the other of HT9 and various refractory alloys. We designed and implemented a rapid method to implant, mechanically test, and microstructurally analyze the 316L, 409, and 420F stainless steels, as well as the diffusion couples. We determined that the micropillar compression dimensions are limited by the ion irradiation parameters and the homogeneity of the samples. Nanoindention, combined with finite element modeling, provide significant insight in a rapid manner that provides adequate first-order comparison between various potential cladding metals. Care does need to be taken to account for surface modifications from both ion irradiation and sample preparation (work hardening). This project has shown that a first-order comparison of cladding materials radiation resilience can be achieved by heavy ion irradiation and small scale mechanical testing. We also learned that a more in-depth, but still rapid,

characterization can occur from the concurrent irradiation of both heavy ion, He, and protons to simulate the effects of displacement damage, He bubble formation, and hydrogen embrittlement, all of which can result from neutron irradiation.

We also developed two unique capabilities for nearly in situ ion irradiation scanning electron microscopy and electron backscatter diffraction (SEM/EBSD) and in situ ion irradiation transmission electron microscopy (TEM). As a result, we have become a leader in the in situ ion irradiation field. This has resulted in an invitation to host the second workshop on the use of in situ TEM/ion accelerator techniques.

We presented this work at a multitude of conferences and are in the process of preparing several manuscripts. We also assisted in the education of two students.

Significance:
The success of this project will provide Sandia with a materials testing platform that will support the development and scientific investigation of structural materials for use in an advanced fast-neutron burner reactors and generation IV nuclear energy activities. The DOE Office of Nuclear Energy (DOE-NE) is keenly interested in the support and success of missions such as the FCR&D and the generation IV reactor development. This project directly addresses technical needs for these programs. In addition, this capability may be used for future programs involving other types of neutron irradiation, including materials for thermal neutron reactors and fusion reactors.

This project has provided Sandia with two new and unique capabilities for characterizing microstructural evolutions as a function ion irradiation conditions. The first in an SEM/EBSD system mounted on an end station of a tandem accelerator providing nearly in situ recording of the texture evolution that occurs during ion irradiation. The second is an in situ ion irradiation TEM that permits real-time nanoscale observation of thin foils during ion irradiation.

Cognitive Stakeholder Modeling for Resource Management
130745

Year 3 of 3
Principal Investigator: V. C. Tidwell

Project Purpose:
A key national challenge is that of formulating policies that motivate needed changes in resource production, allocation, and management. The difficulty lies in selecting policy options that achieve particular goals while minimizing the potential for conflict. Furthermore, the success of a policy decision can hinge more on human factors than on the technical merits of the policy. A priori analysis is largely beyond the reach of current policy tools because: 1) there is a lack of integrated modeling of human decision-making behavior and the environment in which this population operates and 2) collection of primary data for decision-making modeling is costly and time consuming. Our approach is to create a simulation environment that integrates models of stakeholders' decision-making behavior with traditional system dynamics (SD) models of resource constraints and economics, with advanced processes and tools (e.g., automated learning, gaming) for expedited data capture. The technical approach in this project expands modeling and data capture to include factors such as stakeholder desires, needs, biases, and influence. Stakeholders include government authorities, consumers, commercial, and community groups. The resulting model will aid development of candidate solution sets to streamline negotiation processes by providing perspectives to all parties about decision tradeoffs and an early assessment methodology to identify potential conflicts. The benefit is insight for decision makers into alternative perspectives on decision outcomes across a broad range of complex, uncertain, and potentially conflictive situations, including resource scarcity management, energy production, post-disaster recovery, and nuclear waste storage. We are using water planning and management in the Upper Rio Grande basin as an exemplary application.

Summary of Accomplishments:
Technical accomplishments are associated with three broad project objectives: 1) develop a process for capturing relevant information for constructing decision-making models of stakeholders, 2) integrate these decision-making models (agent based models) with system dynamics models of the physical environment, and 3) perform a careful set of experiments to test the contribution of this decision aid within the context of the water planning for the Upper Rio Grande Basin.

Traditional and novel data capture techniques were employed to characterize stakeholder decision-making behavior. Preliminary stakeholder profiles and decision-making models were developed through attendance at public meetings, knowledge drawn from project subject matter experts (SMEs), and perusal of the literature and public documents. Automated data capture coupled with a simulated gaming environment was used to gather additional information through successive model development spirals. Gaming was designed specifically to expose stakeholder values that are key to modeling "irrational agent behavior."

An integrated decision support system was developed employing system dynamics to model the physical environment, agent based modeling to capture stakeholder decision-making behavior, and EMPaSE (Extensible Multi-Paradigm Simulation Environment) to link the two modeling platforms. Through this environment, stakeholders were posed with resource utilization decisions given changes to their local and regional environment. Stakeholder interaction was facilitated through both a traditional modeling interface and a serious gaming interface (developed through collaboration with Intel Corporation).

Experiments with local stakeholders were performed according to three model development spirals. Stakeholders were drawn broadly from local water utility managers, farmers, and environmentalist. In each spiral, stakeholders interacted with the integrated model through the traditional and/or serious gaming interface. Data collected from stakeholder game play was then used to update the decision-making models, which the stakeholders subsequently played against in the following model development spiral. Very positive feedback was gained from stakeholders on this idea, process, and the gaming environment.

Significance:
A simulation environment has been created that integrates decision-making models of stakeholders, traditional system dynamics models of resource constraints and economics, and advanced processes and tools (e.g., automated learning, gaming) for expedited data capture. This combined set of tools and processes is designed to assist decision-making applications for customers in government and industry across a broad range of complex, uncertain, and potentially conflicting situations, including natural resource allocation environmental management; military, medical, disaster recovery and emergency response; and infrastructure planning and coordination. While the system was developed for the particular problem of water allocation in the Upper Rio Grande, it can be adapted and transferred to other equally challenging resource management and allocation problems.

The serious gaming platform demonstrates a radically new means of participatory resource planning. Through collaboration with Intel Corporation, a serious gaming interface featuring water resource trading and allocation in the Upper Rio Grande was developed using Intel's SCIENCEsim gaming environment. The developed interface is a multiplayer, online role-playing "serious game" combining large-scale simulation (e.g., SimCity), with strategy and interpersonal interaction (e.g., Diplomacy). Broad access to accurate and compelling games could: 1) encourage participation of tens of thousands of stakeholders in a given planning decision as opposed to tens of participants that commonly attend meetings today and 2) provide a broader gaming base for exposing, quantifying, and vetting stakeholder behavioral models. In addition, involving and observing stakeholders in the process of developing the game will provide an additional opportunity to elicit information relevant to refining agent models and may point to a more generalized process by which agents can be designed and refined in other situations. Finally, this serious gaming platform will likely be particularly intriguing to the next generation of planners who will soon inherit responsibility for planning and managing our nation's resources.

There are several immediate opportunities to leverage and utilize the integrated DISCERN Analytics Inc. decision platform. The first of these is within the science, technology, engineering and mathematics (STEM) educational community. The serious gaming platform provides an inviting environment to engage students around science, technology, engineering and mathematics. We will pursue this avenue jointly with Intel and will target National Science Foundation (NSF), DOE and large textbook companies like McGraw-Hill. Other opportunities target national security through the lens of resource sustainability. Potential applications involve DOE's climate science mission supporting integrated assessment modeling, particularly as it applies to human response (e.g., purchasing decisions, policy) to climate change. In terms of acute problems, there is the connection to the DHS S&T Directorate and their plans toward the creation of a program around US potable water infrastructure. Finally, there is a new effort involving DOE and the Bureau of Reclamation targeting negotiated settlements and the utilization of associated natural resources by the US tribal community.

Linking Ceragenins to Water-Treatment Membranes to Minimize Biofouling
130748

Year 3 of 3
Principal Investigator: S. J. Altman

Project Purpose:
Biofouling impacts membrane separation processes for many industrial applications such as desalination, wastewater treatment, oil and gas extraction, and power generation. Biofouling results in a loss of permeate flux and increase in energy use. The energy sector is concerned about biofouling as water recycling becomes more and more prevalent. Examples include reuse of cooling water and water used for steam injection for heavy oil extraction. Creation of biofouling-resistant membranes will assist in creation of clean water with lower energy usage and energy with lower water usage.

We are testing the use of ceragenins to create biofouling-resistant water-treatment membranes. Ceragenins are synthetically produced antimicrobial peptide mimics that display broad-spectrum bactericidal activity. While ceragenins have been used on biomedical devices, use of ceragenins on water-treatment membranes is novel.

Summary of Accomplishments:
We have synthesized four different ceragenin molecules for attachment to the membrane surface. We have used three of the molecules to test five different methods for attaching the ceragenins to the membrane surface. The attachment methods are: 1) direct attachment, 2) amine-linked polymer brush, 3) ultraviolet (UV)-grafted polymer brush, 4) silane-linked polymer brush, and 5) silane direct attachment. Of the five attachment methods, staining demonstrates that silane direct attachment leads to the highest density of ceragenins on the surface of the membrane. We have tested membranes that have used methods 2, 3, and 5 for their ability to reduce biofouling as compared to an untreated membrane. The most promising results from this testing showed the amine-linked polymer brush and silane direct attachment methods lead to a 79% and 64% reduction in biofouling, respectively. Additional testing is needed with respect to the repeatability of these results.

We have isolated 47 different biosafety level 1 and 2 species of bacteria from five different water sources relevant to desalination: waste water, brackish groundwater, agricultural drainage, river water, and seawater. Preliminary screening downsized the number of isolates to 12 for further evaluation of their biofouling potential. Further screening demonstrated that most of the 12 isolates grow biofilms with densities in the 10^4 to 10^8 colony, forming units/cm^2 range. The isolates from seawater and brackish groundwater appear to be slower growing than the other isolates. We have filed three patent applications on methods for attaching polymerizable ceragenins and ceragenin-containing copolymers to polymer substrates. This project has also led to additional work related to water-treatment membrane testing and creating biofouling-resistant coatings for marine hydrokinetic devices, renewable sources of energy.

Significance:
The continued security and economic health of the US depends on a sustainable supply of both energy and water. These two critical resources are inextricably and reciprocally linked; the production of energy requires large volumes of water while the treatment and distribution of water is equally dependent upon readily available, low-cost energy. Through creation of biofouling-resistant membranes, this research allows for creation of more clean water with less energy use, completely in concert with Sandia and DOE missions.

Membranes and Surfaces Nanoengineered for Pathogen Capture and Destruction
130749

Year 3 of 3
Principal Investigator: M. D. Nyman

Project Purpose:
Obtaining potable, safe water has always been a challenge for developing countries, and there is also potential for contamination of routinely treated water in developed municipalities. Emerging threats include disinfection-resistant pathogens and pharmaceutical contamination. Furthermore, increasing industrialization and population and mass-produced agriculture means clean water is both consumed and polluted at increasingly higher rates. These sobering issues have both necessitated increased use of challenged water (i.e., surface water instead of groundwater) and expanded interest in advanced materials for more reliable and consistent water treatment.

We are developing advanced multifunctional coatings for water filtration media. These are designed to: 1) retain microbial organisms by chemical affinity rather than size exclusion and 2) self-clean by a combination of photocatalytic decomposition of sorbed contaminants and charge switching of the surface. Both self-cleaning mechanisms are carried out in a controlled fashion by light exposure. The specific water treatment technologies and associated problems we are addressing are the following: 1) micro-organisms such as viruses are too small to filter by size-exclusion, 2) biofouling of water filtration media is a pervasive problem, and 3) disinfection methods are not completely reliable in inactivating infectious contaminants.

The biggest challenge in developing advanced materials for water treatment that can actually be employed is producing something that is cheap enough and/or results in revolutionary improvement in performance, reliability, etc. To address this challenge, we are applying some effort towards utilizing inexpensive materials that already have commercial applications. On the other hand, to address our desire to produce meaningful scientific developments, we are also dedicating efforts toward novel materials and advanced methods of characterization (i.e., atomic force microscopy, [AFM]).

Summary of Accomplishments:
As a final product of this project, we have produced a hybrid nanoengineered surface that can capture and destroy microorganisms, such as the bacteriophage that was used as a model contaminant. This model contaminant is very small (30 nm) and thus presents a bigger challenge than if a smaller pathogen were utilized (i.e., the capture is by chemical or physical adhesion, not just settling out of solution). The ‘glue’ portion of the hybrid material is an inorganic, cationic molecule that electrostatically binds to both the anionic photocatalytic material as well as to the anionic contaminant (most contaminants are anionic, thus must be engineered this way). The photocatalytic portion is titanate sheets that adhere well to a flat surface as a monolayer. We have developed our own cost-effective method to synthesize these, and a patent is currently being written — since the sheets have applications beyond this particular application. We have demonstrated adsorption of the pathogen to the surface functionalized with the hybrid material, followed by photocatalytic destruction. Ways to improve the potency of the photocatalytic material included addition of phosphate and addition of peroxide. The phosphate provides a shift in the bandgap to closer match the ultraviolet (UV)-source for photocatalysis and the peroxide provides free radicals at the surface of the materials for enhanced oxidation of organics. All these results have been published. In addition to this application, we have found that delaminated titanates are ideal for capturing rare earths out of a solution containing a mixture of ions. This impacts different applications than the original idea of this project and, thus, provides a foundation for new directions of research.

Significance:

The project will be deemed successful if multiple composite coatings are developed that can perform one or more of the functions optimally: pathogen capture and destruction and desorption. Not only can these surfaces be employed in multiple media (i.e., membranes or granular filter beds) for water treatment, but also for any application that requires capture, detection, destruction or release of pathogens. Some specific examples include preconcentrators for detection, anti-pathogenic surfaces for commercial products, or hypoallergenic surfaces for medical applications. This work also has potential in the arena of national security, concerning biological warfare. Considering the project's two goals, this project satisfies DOE's core missions of both national security and scientific innovation and discovery.

Refereed Communications:

T.A. Stewart, M. Nyman, and M.P. deBoer, "Delaminated Titanate and Peroxotitanate Photocatalysts," *Applied Catalysis B Environmental*, vol. 105, pp. 69-76, June 2011.

Modeling of Advanced Nuclear Fuel Pins
130750

Year 3 of 3
Principal Investigator: T. J. Bartel

Project Purpose:
The core of a fast neutron burner or breeder reactor during a transient event represents one of the most complicated environments possible for structural materials. The ability to simulate the change in the microstructure and the resultant change in mechanical properties of the materials in this environment is vital to predictive models for the safety and performance of the reactor as a whole. Current models can simulate microstructural evolution such as coupled grain growth and bubble migration, but are not directly informed by the mechanical stress and temperature fields. The evolution in microstructure and mechanical phenomena such as cracking, creep, and swelling are intimately related and must be included together for high-fidelity predictive simulations. This project is developing algorithms and capabilities to incorporate the necessary multiple, coupled physical phenomena into a code based on the material point method (MPM). Microstructural evolution such as grain growth and restructuring are handled by calibrated Monte Carlo (cMC) models while plasticity is handled by grain-level continuum crystal plasticity theory. These major methods will be further developed to include new physics such as fission gas bubble at the mesoscale, solid mass transport and fracture. The core challenge and deliverable of this project will be to combine the cMC and plasticity methods within a MPM based code to provide a detailed physics-based simulation capability of the thermomechanical behavior of a fuel pin, that is, both fuel and clad, to a transient thermal environment in a computationally efficient timeframe.

The direct, time-accurate coupling between the different length scales coupled with the mechanical response has never been demonstrated. We are attempting to do this in a relevant scale 3D simulation of the fuel rod during a transient to directly compute the clad strain. Computational performance may represent the critical item from obtaining a useful simulation capability; we continually investigate algorithms to address this concern.

Summary of Accomplishments:
The primary accomplishment during this year was adding a fully implicit time integration scheme to the MPALE (Material Point Automated Lagrangian Eulerian) code. This was accomplished by building an interface to the Sandia-developed solver package, Trilinos, and coupling that into the previous explicit time-integration strategy used in MPALE. This new code is called iMPALE and can either be run in an explicit or implicit time mode. The focus on the implicit time integration was for the mechanics to overcome the explicit time step limitation of the inertia terms. As a bonus, we have included an implicit diffusion equation solver to be used for thermal (conduction) solutions, as well as atomic gas and vacancy transport. The implicit time integration solver for the mechanics was required to allow a creep model be used for nuclear fuel and clad materials.

A secondary accomplishment for the density functional theory component was the development of a fast approximate strategy to obtain the influence of a strained lattice on the diffusion of gases. This is to address differences between thermal and mechanical strains on the transport of atomic species: fission gas products.

Finally, the iMPALE was “cleaned up” and a user manual prepared to facilitate its use for further code development and applications.

Significance:

Sandia has had a longstanding and well-established role in safety technologies for nuclear reactors. We also have the only operating reactor in the DOE complex that can perform these experiments. The development of these computational capabilities will allow us to support transient fuel experiments and maintain our unique capabilities in this area. In addition, many NNSA technologies will benefit from this project, such as ceramics for microelectronic packaging, solder joints, piezoceramic materials (PZT) ceramics, cermets, microsystem technologies, and solid oxide fuel cells. This development effort is being used for two FY 2012 projects: an experimental project investigating the mechanical properties of nuclear fuel clad material subject to long term storage, and a DOE/National Aeronautics and Space Administration (NASA)-funded effort to analyze the safety issues of launching nuclear material (radioisotope thermoelectric generators) into space for space science missions. This second effort investigates the mechanical properties of PuO_2 with helium bubbles in the grain boundaries from alpha decay. Finally, a collaborative effort between Sandia and CEA-Saclay (French) has been initiated based on the capabilities developed in this project.

Refereed Communications:

L. Zhang, R. Dingreville, T. Bartel, and M.T. Lusk, "Hybrid Monte Carlo Simulation of Stress-Induced Texture Evolution with Inelastic Effects," *Metallurgical and Materials Transactions,* vol. 42, pp. 575-581, March 2011.

L. Zhang, R. Dingreville, T. Bartel, and M.T. Lusk, "A Stochastic Approach to Capture Crystal Plasticity," *International Journal of Plasticity*, vol. 27, pp. 1432-1444, September 2011.

R. Dingreville, K. Shaheen, B.J. Lewis, W.T. Thompson, and T. Bartel, "Towards Integrating Mesoscale Models of Microstructural Evolution of Uranium Dioxide Fuel within Continuum-Scale Models of Thermo-Mechanical Behavior of Nuclear Fuel Elements," to be published in the *Journal of Nuclear Materials*.

R. Dingreville and T. Bartel, "Crystal Plasticity in the Material Point Method Framework," to be published in the *International Journal of Plasticity*.

Scalable Microgrid for a Safe, Secure, Efficient, and Cost-Effective Electric Power Infrastructure
130752

Year 3 of 3
Principal Investigator: A. L. Lentine

Project Purpose:
Distributed renewable energy generation is a key component in transforming society from its reliance on fossil-fuel based energy to a carbon-neutral, sustainable, and secure energy infrastructure. However, the current power grid cannot handle a significant penetration of renewable generation (wind, solar) because of fluctuations in the supply of electricity from changing weather conditions, bidirectional power transport in a distributed network, and safety and security issues associated with working on a grid with numerous power sources.

We are researching a fundamental shift in the management and distribution of electricity at the home, local, regional, and, ultimately, national scale. This consists of developing a “micro-grid” that is scalable at multiple levels (e.g., homes/businesses, neighborhoods, cities, and regions). Our new power grid architecture uses information networks to enable real-time cooperative generation, intelligent metering, and load management functions to provide decentralized coordination of potentially millions of distributed generation sources and loads in an active, adaptive virtual “super-grid” that is stable, secure and sustainable.

The power industry is looking to extend the current operational model as far as possible with even larger geographic (balancing) areas, improved forecasting in conjunction with large supplies of backup power and energy storage. However, both renewable energy portfolio standards and equivalent standards for military bases will push renewable energy generation over the point at which the system cannot effectively absorb this variation over all times. Importantly, we believe that the requirements for fast power flow control, reactive to the changing renewable resources, requires a new approach that consists of distributed, decentralized closed loop control systems that monitor network parameters (power, voltage, current, power factor) and control power flows (storage, loads, generation) accordingly. Our approach is very different from the direction in which the smart grid research and development is headed.

Summary of Accomplishments:
An intelligent electrical outlet and demonstration of a group of these outlets that can collectively adjust their loads in response to available electric power measured from a photovoltaic source was developed. Also developed were initial concepts for novel electromagnetic sensing from high-voltage power lines without the usual step-down transformers used today.

Significance:
Transitioning the grid from its current centralized structure to a distributed intelligent grid enables the transition of society from fossil-fuel based energy to a carbon-neutral, sustainable, and secure energy infrastructure with reduced dependence on foreign oil imports and is very much consonant with DOE initiatives. It lessens the need for increased use of nuclear power, its generated waste, and the enhanced security required to reprocess waste into fuel. Its distributed nature provides intrinsic-security of power generation, distribution, and storage.

Vulnerability of Multi-Network Infrastructure to Cascading Failure: Design of Robustness to Novel or Orchestrated Perturbations
130766

Year 3 of 3
Principal Investigator: W. E. Beyeler

Project Purpose:
Taken as a whole, critical infrastructure is a network of dynamically interacting systems of systems designed for the flow of information, energy, and materials. Under certain circumstances, disturbances from a targeted attack or a natural disaster can cause cascading failures within and between infrastructures that result in significant service losses and long recovery times. Reliable interdependency models that can capture such multinetwork cascading do not exist. Individual infrastructures are systems designed to produce and distribute commonly used resources; many important interdependencies among infrastructures arise from the relationships of resource consumption and production among them. The purpose of this project is to develop a general understanding of infrastructure interdependencies through an abstract model of systems composed of specialized resource users. When applied to specific systems, the model becomes a tool for identifying the process and features that might lead to system-spanning disruption, and to design changes to the system to moderate or prevent such events.

Summary of Accomplishments:
This project developed and applied a general model for the interaction of large numbers of individual entities whose properties and dynamics are suited to the analysis of infrastructure systems, but are not limited to those systems. Several novel modeling constructs were created in the course of this development, including parsimonious models for behavior and open-ended models of technological innovation. We have used a Java-based implementation of this model to study the behavior of several disparate systems. These studies have demonstrated the flexibility of the model, but have also revealed unexpected system behavior, such as competitive exclusion and abrupt transitions in strategic viability with increasing resource scarcity. The results and surprises produced in these initial applications seem particular to the modeled systems. For example, the observation that a diversity of entity types in a production network leads to a greater chance of instability depends on constraints placed on the analysis, such as preserving the total number of entities and adopting a simple generative mechanism for production networks. This observation is not likely to generalize to all systems covered by the model. Some general features may eventually be discovered; however, only a small number of simple systems have been investigated so far.

Two application areas are immediately attractive. Both are extensions of example applications created during the course of the project. First, a simple model used to look at inter-regional trade effects has obvious application to problems in international economic relations and to international relations more generally. Second, the preliminary model of production network stability was developed as an initial step in modeling the robustness and failure characteristics of real industrial production systems. Insights from such modeling can be a great help to the various interests and institutions exposed to risks from these systems.

Significance:
This work ties directly to Sandia's DOE/DHS/national security missions. It allows analysis of the vulnerabilities of our national critical infrastructure including system interdependencies. It develops new understanding of how the worst types of failures can be initiated by an adversary and provides a framework for how to evolve the systems to prevent failure cascades. Because the model is being built

in a generic framework, it is readily applicable to any complex adaptive system of systems and, thus, has applications to the work of many of government agencies.

Complex Adaptive Systems of Systems (CASoS) Engineering and Applications to the Global Energy System (GES)
134529

Year 3 of 3
Principal Investigator: W. E. Beyeler

Project Purpose:
Complex adaptive system of systems (CASoS) is ubiquitous. They include cities, infrastructure, government, armed forces, nations – in short, systems that are socioeconomic-technical in nature. As a national laboratory with an engineering mandate, nearly every important problem that we confront is within a CASoS; problems include nuclear stockpile management, nonproliferation, energy surety, and critical infrastructure protection. We must recognize this CASoS context to properly pose and solve problems while not producing unintended consequences: that they are feasible solutions, robust to uncertainties, and enhance system resilience. Of essential importance to this engineering process is the actualization of the solution within the CASoS, a step that is often neglected. The purpose of this project is to develop a general CASoS engineering framework for the definition, design, testing and actualization of solutions within CASoS and a CASoS Engineering Environment for the implementation of the Framework. This development must be done through focus on high priority, specific applications while keeping an eye on the general. We chose the global energy system (GES) as our CASoS of application. The GES contains both complex earth and complex adaptive human systems including economic, socio-political, and technical systems. The GES is currently the nation and humankind's highest priority, largest, most important CASoS.

Summary of Accomplishments:
We designed the Phoenix Pilot as a crucible from which systemization of the new discipline of CASoS engineering could emerge. Using a wide range of applications, Phoenix built both theoretical foundations and capability for: the integration of applications to continuously build common understanding and capability; a framework for defining problems, designing and testing solutions, and actualizing these solutions within the CASoS of interest; and an engineering environment required for "the doing" of CASoS engineering. In a secondary objective, we applied CASoS engineering principles to build a foundation for design in context of global CASoS.

Significance:
DOE's overarching mission is to advance the national, economic, and energy security of the United States. The GES is the arena in which both DOE and Sandia carry out their missions. The GES is a CASoS, but it is rarely treated as such. Bringing CASoS approaches and techniques to analysis of the GES will improve Sandia and DOE's ability to optimally perform their respective missions.

Advanced Battery Materials for Improved Mobile Power Safety
141614

Year 2 of 3
Principal Investigator: C. Orendorff

Project Purpose:
The objective of this project is to develop abuse-tolerant inactive materials for lithium-ion batteries for transportation applications. While the electrolyte and separator materials of lithium-ion batteries are considered "inactive" materials because they do not directly participate in the electrochemistry of a functional cell, it is well understood that the electrolyte and the separator have significant impact on the abuse tolerance and thermal stability of these cells. The primary concerns with these materials include flammability of the electrolyte, degradation of the electrolyte to generate a large volume of CO_2, and incomplete separator shutdown at modest temperatures (< 150 °C) leading to cell thermal runaway. Most conventional approaches to improving the abuse response of these materials include using additives in electrolytes (e.g., flame retardants, stabilizers, etc.) or coating polymer separators with ceramics. However, these approaches do not solve the fundamental problems associated with these materials. Our approach is to mitigate these potential hazards by shifting the focus to utilizing new materials. We have used electrolyte salts and solvent systems that: 1) have no flash point and are inherently less flammable and 2) are more thermally stable to minimize the amount of CO_2 decomposition gas generated by each cell. We have also demonstrated the use of lithium-ion battery separators based on teraphthalate polymers that are more thermally stable than conventional poly(ethylene)/poly(propylene)-based conventional separators. This project is unique in that it utilizes innovation in materials science, materials processing/development, fundamental characterization, and macroscale testing to develop and verify inherently safer battery materials for the transportation industry.

Summary of Accomplishments:
The key accomplishments for FY 2011 include determination of electrolyte flammability, characterization of fluorinated EC (F-EC) containing electrolytes, cell performance measurements with hydrofluoroether (HFE) electrolytes, fabrication of naphthalate-based separators, direct coated ceramic (DCC) separators, and performance characterization of these separators in lithium-ion cells. Flammability measurements on HFE electrolytes and cells with HFE electrolytes show no ignition to external spark upon cell venting for compositions of 50% HFE co-solvent. This is a significant result for Li^+ cells when compared to the conventional all-carbonate solvent electrolytes that ignite immediately after cell vent and do not self-extinguish until all carbonate fuel is consumed. Vent temperatures for cells with HFE electrolytes are increased from 160 °C to 190 °C, which is a measurable improvement in safety margin for Li^+ cells. Cells with HFE electrolytes show comparable performance to control cells in terms of capacity (1.2 Ah) and capacity retention (> 85%) over 200 cycles with no indication of corrosion or chemical reactivity over time. Calorimetry on the F-EC electrolyte with $LiPF_6$ shows comparable onset degradation temperature and moles of decomposition gas as non-fluorinated EC.

We have made significant progress on the development of terephthalate- and naphthalate-based separators. We have improved processing conditions to prepare separators that are 25-35 μm thick and permeability up to two orders of magnitude less than that of commercial separations. The performance of these materials is comparable to that of commercial separators in terms of capacity retention and rate capability. We have also built a processing platform to process separators for 18650 cells (100 cm^2) and that work will begin in FY 2012. Moreover, we have had some good initial success in direct coating separators on electrodes. This work had implications in reducing processing time, cost, and offers a potential improvement in the safety of cells designs.

Significance:

The accomplishments of this project will contribute to Sandia's mission as well as ST&E roadmapping efforts in transportation energy. This project will also have an even greater impact on the broader S&T community. For example, the electrolyte flammability testing that has been developed as part of this work could potentially be adopted by a number of test manuals (SAE J2464, UL, USABC, etc.) en route to becoming a certified test procedure that would influence how future batteries are evaluated. This type of testing could be rolled into follow-on work for others (WFO) or cooperative research and development agreement (CRADA) projects with outside partners who are interested in evaluating other electrolyte systems. Moreover, FY 2013 will focus on obtaining intellectual property for our separator materials technology that could be licensed to an industrial partner for manufacturing and scale-up.

In general, the results from FY 2011 will be used to make recommendations about materials choices in lithium-ion cells that have the potential of improving their overall safety. This work will be leveraged using our comprehensive understanding of safety and abuse response of cells, our ties to the DOE Office of Vehicle Technologies (OVT) missions (USDrive, US Automotive Battery Consortium, and Advanced Battery Research), and association with the general battery community (automotive industry, developers, etc.) to implement system improvements. Given our unique position of being an applied testing laboratory, combined with fundamental research interests, makes us well suited to integrate these materials into actual systems and demonstrate their performance. Presenting results from this work to the community lead to a great deal of visibility for this project.

From a technical perspective, electrolyte flammability and low-temperature instabilities in separators and electrolytes represent potential failure mechanisms that may not be fully mitigated through engineering controls in lithium-ion systems for transportation. These are inherent materials chemistry phenomena that can be fully addressed at the materials scale. This is largely overlooked by the community and puts Sandia in a leadership position in understanding these safety issues and offering solutions.

Refereed Communications:

G. Nagasubramanian and C.J. Orendorff, "Hydrofluoroether Electrolytes for Lithium-Ion Batteries: Reduced Gas Decomposition and Nonflammable," *Journal of Power Sources*, vol. 196, pp. 8604-8609, June 2011.

Bridging the Gap between Atomistic Phenomena and Continuum Behavior in Electrochemical Energy Storage Processes
141615

Year 2 of 3
Principal Investigator: S. K. Griffiths

Project Purpose:
One of the most significant impediments to advances in electrochemical energy storage lies in the gap between fundamental understanding of atomistic phenomena and our understanding of the impact of these phenomena on system performance at device scales. Atomistic models (density functional theory [DFT], molecular dynamics [MD], Monte Carlo [MC]) provide insight into such phenomena along with a means of quantification, but such models are too computationally intensive to address device-scale behavior. Similarly, device-scale insight for design and optimization can be obtained through continuum models that are sufficiently fast, but these models account for only the simplest atomistic phenomena. There is thus a large gap between our ability to develop fundamental understanding and our ability to use this understanding to make rapid advances in energy storage technologies. The goal of this project is to help bridge this gap through an innovative synthesis of atomistic and continuum approaches in which atomistic phenomena are captured through fast reduced-order integral methods that can be imbedded into continuum-like models describing device-scale behavior.

Our approach to bridging this gap is a synthesis of atomistic and continuum methodologies in the form of reduced-order integral equations derived from DFT. In this novel synthesis, transport and reaction of chemical species are described by partial differential equations similar to those currently employed in continuum models, but the chemical potential and constitutive relations normally used in these models are replaced by integral equations describing underlying atomistic processes. Through this approach our solutions will forego unnecessary detail at atomistic scales to greatly reduce execution times while still accurately representing the impact of atomistic phenomena on macroscale behavior in a manner that is rigorous and physics-based. Success in this project will, therefore, represent a major advance in our ability to incorporate atomistic electrochemical phenomena into device-scale simulations, enabling accelerated innovation in materials and devices for electrochemical energy storage.

Summary of Accomplishments:
We successfully derived a coarse-grained DFT suitable for incorporation of atomistic physics into traditional continuum modeling. This approach yielded molecular-scale ion density distributions and capacitance profiles nearly identical to those of traditional DFT, while providing more than ten-fold reductions in grid spacing and thousand-fold reductions in CPU time. To help guide and validate this approach, we have since used large-scale atomic/molecular massively parallel simulator (LAMMPS) to perform a sequence of increasingly challenging MD simulations of fluids and electric double layers confined within narrow channels. Although our MD and DFT results are in excellent agreement for uncharged fluids, we have discovered significant discrepancies for charged species in both the ion distributions and electric fields within the electric double layer (EDL). Because our DFT results agree with published MC simulations of the EDL, we have focused on and explored potential problems with MD concerning the treatment of anisotropic Coulombic interactions. We now believe these interactions are widely treated in an inaccurate manner and are working to develop a new methodology. In addition to these DFT and MD efforts, we have completed first steps toward our second major goal of incorporating EDL structure into models of viscosity, diffusivity, and electrophoretic mobility. Previous work by others, based on Chapman-Enskog theory and MD simulations of hard-sphere fluids, provided analytical expressions describing the variation of viscosity and diffusivity with temperature and local

density. We have used these expressions to compute viscosity and diffusivity distributions based on our coarse-grained DFT density profiles for various channel widths. Cross-channel averaging of these profiles has produced mean values of viscosity and diffusivity that generally agree well with published MD simulations for channel widths ranging downward to a width of two or three molecular diameters. A transition to alternative modeling of single-file diffusion is probably required to address the smallest scales.

Significance:

This project directly supports the high-level DOE goals of reducing petroleum imports, incorporating intermittent renewable sources into our electrical grid, improving grid reliability and security, and dramatically reducing carbon emissions. It addresses these goals through improved understanding of electrochemical energy storage and improved computational tools for the design of advance batteries, capacitors, and fuel cells. The project additionally supports the DOE/NNSA mission by providing new expertise and computational tools relevant to electrochemical corrosion processes and advanced power supplies for nuclear weapons. Finally, this project supports DoD goals to provide secure large-scale power and energy-storage systems for critical base operations.

First-Principles Flocculation as the Key to Low Energy Algal Biofuels Processing 141617

Year 2 of 3
Principal Investigator: J. C. Hewson

Project Purpose:
Algal biofuels have the potential to substantially contribute to energy diversity if certain barriers can be overcome. A significant hurdle is the energy/cost associated with harvesting and dewatering algae. In theory, algae flocculation could drastically lower harvesting costs, but flocculating mechanisms that are reliable, effective, and efficient have yet to be identified. The propensity of algae to flocculate can be related to the properties of the algae surface and its interaction with the water surrounding it. Of key importance is the tendency of algal surfaces to develop a negative charge and the ability of ions in the water to alter the resulting electric double layer. We are pursuing a fundamentally different scientific approach to understanding the algae-water interface and its dependence on water chemistry and algae life cycle. The objective is to identify conditions favorable to flocculation that take advantage of algal pool chemistry (salinity, pH, etc.), low-tech flocculating agents (clays, bubbles, etc.), and the influence of fluid dynamics on the floc evolution. The project will employ an iterative sequence of theoretical predictions leading to hypotheses to be tested experimentally to develop a comprehensive understanding of the algae-water interface physics at the scale of the electric double layer formed on the algal surface and at the scale of inter-algae forces. The interrelation between fluid flow and sticking affinity in evolving floc dynamics is also being studied with combined experimental measurements and predictive modeling that draws upon and reinforces the understanding developed at the scale of the algae surface. A combination of highly controlled experimental environments and those more typically experienced in scaled-up production systems are being studied to identify scaling challenges. The objective is a map of the flocculation potential as a function of water chemistry and low-cost additives and a predictive model of flocculation dynamics given that flocculation potential that could be applied in the future planning of algal resource development.

Summary of Accomplishments:
In the past year, the project shifted from developing capabilities through improving the understanding of flocculation and on to mapping conditions for reliable flocculation. Cultivation capacity improved through the development of a photobioreactor system for larger-scale cultivation, allowing us to investigate links between water chemistry and fluid mixing in floc growth. We are now investigating both freshwater and saline algal species. We conducted a series of titration measurements to characterize the algal surface and developed surface-complexation models to describe algal surfaces in the presence of varying water chemistry. These algal surface models are developed in the context of open-source software packages and we are publishing exemplary input files to guide future users.

We conducted a sequence of measurements of fresh-water and saline-water flocculation as functions of flocculant and pH, leading to a first flocculation-potential map for algae that resolves some of the key issues related to combined pH and flocculant effects that have clouded interpretation and comparison of literature data. This map was developed with the combined analysis through surface-complexation models (that indicate regions of charge-induced destabilization) and population-balance models (that indicate regions where rapid collisions reduce flocculant requirements) to identify flocculation regimes. This combined analysis is also allowing us to relate performance of conventional flocculants to low-cost flocculants.

We have initiated a combined experimental and modeling study of the effects of shear on floc growth and structure through the application of the particle-dynamics code, large-scale atomic/molecular massively parallel simulator (LAMMPS), and measurements in a Couette device constructed for this project. This work has added JKR (Johnson-Kendall-Roberts) potentials (allowing floc restructuring through finite-resistance rolling, twisting and breaking modes) and additional flow field models to LAMMPS.

Significance:
Energy security is one of the key missions of DOE. Factors such as depletion of worldwide petroleum-based energy resources, coupled with increasing competition for global energy supply from emerging economies such as China and India have created an energy challenge in the US. Biofuels are a viable alternative that can address this energy challenge if they can be produced abundantly. Algae represent a domestic resource stream for biofuels that has potentially less impact on land and water suitable for crop production than other sources. This project addresses key technical hurdles in realizing algae as a resource for substantial energy production. It does so by mapping the conditions for efficient extraction of algae from the culture medium. Further, this project develops capabilities in the form of physics-based models built largely around open-source tools that will enhance the ability of practitioners to develop more specific effective-flocculation mappings for their own operating environments.

Beyond algal biofuels, this project increases the scientific understanding of dilute solid-liquid separation processes relevant to industrial separations and water treatment among other areas. It brings together combined experimental and modeling capabilities to identify enhanced efficiencies in these processes that have energy-saving and resource-saving potential.

Refereed Communications:
N.B. Wyatt, L.M. Gloe, P.V. Brady, J.C. Hewson, A.M. Grillet, M.G. Hankins, and P.I. Pohl, “Critical Conditions for Ferric Chloride-Induced Flocculation of Freshwater Algae,” *Biotechnology and Bioengineering*, vol. 109, pp. 493-501, September 2011.

Novel Room Temperature Synthesis of Nuclear Fuel Nanoparticles by Gamma-Irradiation
141618

Year 2 of 3
Principal Investigator: T. M. Nenoff

Project Purpose:
This project continues our research into the synthesizing and characterizing depleted uranium (d-Uranium [dU])-based fuel surrogate nanoparticles at room temperature. This low-temperature synthesis virtually eliminates any volatility, which is particularly important for syntheses including highly volatile Am (melting point 994 °C). Metallic and oxide alloys of varying compositions can be produced. Radiolytic formation of nuclear fuel nanoparticles is a completely novel approach to thinking about fuel materials synthesis. This research uses gamma-irradiation for the radiolysis of solvating water to perform room temperature synthesis of metal alloy and oxide nanoparticles (NPs). The radiolysis is performed at the Sandia Gamma Irradiation Facility (GIF) ^{60}Co source ($3x10^6$ rad/hr).

Our primary focus is on the novel synthesis and characterization of surrogate fuels nanoparticles and their formation to bulk fuels. We are studying the nanoparticle formation (through the room temperature chemistry of radiolysis and its effect on metal(s) solutions), composition (through use of proper surrogates, including dU and lanthanides [Y, Eu, and La] for americium), and stability (effects of dose and dose rate on nanoparticle growth) of the surrogate fuels. Production of bulk fuels from nanoparticles is of equal importance to this project. Both metal and oxide NPs have been utilized for sintering studies. We will research new powder processing techniques to achieve high-density (85 to 90%) bulk fuels. As a result, large quantities of fuels for research purposes will be produced for accelerated advanced nuclear fuel development.

The high creativity and innovation of this project are observed in both synthetic methods and goals: 1) low-temperature synthesis and sintering conditions mean that there is no volatility of fuel components, 2) there is high reproducibility of the products as pure/homogenous phases, and 3) an inexpensive method is developed to make research quantities of fuel surrogates for science-based approaches needed by DOE's Office of Nuclear Energy (NE) Fuel Cycle R&D. We plan to leverage successes from this basic research, proof-of-concept project to assist basic research for DOE/Office of Science (OS) and/or the applied research implicit in DOE/NE-fuels missions.

Summary of Accomplishments:
We accomplished our milestones for FY 2011 and have started on milestones for FY 2012. Our invited review article, "Nanoalloys by Radiolysis," is in review. We successfully synthesized dU metal and dUO_2 nanoparticles, and characterized them by ultraviolet-visible spectroscopy (UV-Vis), transmission electron microscopy (TEM), high resolution TEM/energy dispersive x-ray spectroscopy (HRTEM)/(EDS). All reactions are salt-type (chloride/nitrate) and pH dependent.

We studied dUO_2 nanoparticles formation by radiolysis. The NPs (5 nm) were formed with maximum yield in aqueous reactions of $UO_2(NO_3)_2$-$6H_2O$ and isopropanol, pH=4, 5.5 rad/s, in10 days. Sintering temperature was determined to be 600 °C, a 700–1000 °C reduction in temperature rather than bulk. Manuscript is in preparation for *Chem. Mater*; presented at Spring 2011 American Chemical Society, 2010 Fall Materials Research Society.

We are currently focused on U-alloy NP formations. Aqueous solutions of UCl_4 and polyvinyl alcohol (PVA) organic in pH=1 yields maximum crystalline NPs (< 3 nm). HRTEM and EDS indicate crystalline U (gamma phase) can be formed. With time (7days, in air), NPs transform to UO_2. Surface modification, organic concentration (PVA) studies indicate induced stability of U NPs. NP aging is focus of ongoing work. Initial alloy NPs of U-La (e.g., La, Eu, Nd) have been confirmed by TEM and EDS.

We applied ab-initio molecular dynamics technique and Hubbard DFT+U augmentation to calculate the redox potentials and hydration structures of bare U(III) and U(IV) ions in water, and U(III) and U(IV) ligated with 3 Cl^- ions. Reduction of U(IV) to U(III) is predicted at –0.70 V (experimental –0.52 V) and $U(IV)Cl_3/U(III)Cl_3$ is estimated at –1.78 V, strongly shifted from the bare U(IV)/U(III) value. A theoretical/experimental effort will be used to design ligating ions that diminish the voltage needed to reduce salt to U nanoparticles.

We have developed algorithms to simulate microstructural evolution during differential sintering under applied stress; algorithms validation is in progress. Based on our experimental data and literature review of grain growth and sintering, particle rotation has been eliminated as a sintering mechanism.

Significance:
This project addresses Sandia's mission in the areas of nuclear fuels, intrinsic and global security. In particular, it focuses on Sandia's interests in developing novel nuclear fuel systems via new fuel alloy/oxide phases for DOE/NE-Fuels Campaign needs. It also addresses intrinsic and global security by developing a method of introducing tags in fuel alloys for use in verification and safeguard systems (transparency and safe expansion of nuclear energy).

Refereed Communications:
T.M. Nenoff, B.W. Jacobs, D.B. Robinson, P.P. Provencio, T,-Y. Huang, and D. Hanson, "Low Temperature Sintering Uranium Oxide Nanoparticles Synthesized via Radiolysis," to be published in *Chemistry of Materials*.

K. Leung, D. Jiao, S.B. Rempe, and T.M. Nenoff, "First Principles Calculations of Niq^+ and $Ni2q^+$ Redox Potentials and Dimerization Free Energies in Water," *Journal of Chemical Theory and Comput*ation, vol. 7, pp. 485-495, January 2011.

Programmable Nanomaterials for Reversible CO_2 Sequestration
141619

Year 2 of 3
Principal Investigator: B. C. Bunker

Project Purpose:
The purpose of this project is to adapt nature's primary CO_2 sequestration processes into an artificial setting. The DOE has set targets for cheaply and reversibly removing one billion metric tons of CO_2 from the atmosphere per year to mitigate the contribution to global warming associated with the burning of fossil fuels. Technologies that exist for scrubbing CO_2 from coal fired power plant effluents alone will not be sufficient to moderate increases in atmospheric CO_2. A means for removing CO_2 from the atmosphere is needed. In nature, much of the CO_2 being produced is already being removed via: 1) partitioning of CO_2 into water (i.e., the oceans) and 2) biological processes (i.e., photosynthesis). This project is exploring duplicating some of nature's reversible CO_2 sequestration processes by: 1) utilizing water as the capture agent, 2) utilizing enzymes such as carbonic anhydrase to promote the capture and release of CO_2 from water via the reversible conversion of relatively insoluble CO_2 gas into highly soluble carbonate ions, and 3) utilizing programmable polymers to reversibly switch the solution pH to mediate CO_2 solubility and/or enzyme activity.

Summary of Accomplishments:
Significant progress was made on each of the four major tasks on this project aimed at exploring the use of nanomaterials to program water for the reversible sequestration of CO_2, including the following:

- Programmable Polymers: The first programmable pH buffer system for promoting the loading and unloading of CO_2 from water was developed based on a copolymer of poly(n-isopropylacrylamide) and polyacrylic acid. Tests conducted in water showed that this copolymer can be switched reversibly with temperature to produce a pH range that is appropriate for CO_2 loading/unloading procedures. Tests show that CO_2 unloading is extremely efficient. However, the tests also show that extensive unloading introduces hydrophilic ionic groups that interfere with the phase transition required to reload with CO_2.
- Programmable Enzymes: Tests were conducted on commercial carbonic anhydrase to determine optimum conditions for CO_2 loading. Results confirm that the enzyme is highly active (i.e., reaction rates are diffusion controlled) and that small pH changes can be used to switch the enzyme between loading and unloading cycles.
- Theory/Modeling: Models developed to understand the mechanisms by which CO_2 is converted into carbonate ions were extended to understand the same conversion process as activated by the active site in the enzyme carbonic anhydrase. Results from these models are being used to help guide the development of new strains of carbonic anhydrase for use in artificial CO_2 loading/unloading processes.
- Process Development: A small-scale process development "test bed" was designed and built to enable scientists to evaluate different process flow schemes for CO_2 loading/unloading using programmable polymers and/or enzymes. The system contains interchangeable process "modules," components for gas and fluid handling, thermal management, and a range of renewable energy sources (including solar).

Significance:
The ability to cheaply capture CO_2 from the atmosphere is a critical component of the DOE's strategy to mitigate global warming while allowing the expanded utilization of North American reserves of coal,

oil, heavy oils, tar sands, and even biofuels. Atmospheric capture would allow us to address this critical environmental issue without requiring the cooperation of other users of fossil fuels such as China.

Refereed Communications:

J. Dian, and S.B. Rempe, "CO_2 Solvation Free Energy Using Quasi-Chemical Theory," *Journal of Chemical Physics*, vol. 134, p. 224506, June 2011.

Radionuclide Transport from Deep Boreholes
141668

Year 2 of 3
Principal Investigator: P. V. Brady

Project Purpose:
Disposal of deep (>3 km) boreholes could be a relatively inexpensive, safe, and rapidly deployable strategy for disposing America's nuclear waste if: 1) the thermal-hydrologic-chemical-mechanical (THCM) controls over borehole stability and radionuclide transport up/along the borehole and through salinity-stratified groundwater could be predicted with sufficient confidence; and 2) borehole backfills and seals could be designed to provide intrinsic chemical and physical resistance to the movement of water and long-lived radionuclides, including the most mobile isotope of concern, iodine-129. While suitable crystalline host rocks are ubiquitous throughout the country and the technology for drilling deep boreholes is reasonably common in the oil and gas industry, the fundamental science of borehole stability and borehole chemical transport is lacking. This knowledge gap exists, in part, because the primary emphasis of US repository science the past thirty years has been mined geologic disposal at Yucca Mountain, Nevada.

We will build the fundamental science of borehole stability and chemical transport by: 1) developing a "first-of-its kind" coupling of THCM codes that can predict mechanical stability, heat flow, fluid movement, and chemical transport under borehole conditions and 2) establishing the experimental and theoretical basis for optimizing borehole seals and backfill design to limit vertical transport of radionuclides up the borehole.

Summary of Accomplishments:
In FY 2011, we achieved the following:

1. Our work was cited positively by the President's Blue Ribbon Commission on Nuclear Waste.
2. We completed the borehole reference design (emplacement depth, separation distance, drilling methodology, backfill strategy, etc.).
3. We performed thermal-hydrologic-mechanical (THM) modeling of borehole temperature profiles to support the reference design and backfill analysis.
4. We completed the draft borehole backfill analysis.
5. We fabricated a bismuth oxide sorbent with a Kd > 100 ml/gm in a 0.5 molar NaCl solution at 90 °C.
6. Our team submitted one patent, two invention disclosures, one peer-reviewed article (with MIT collaborators) in press in *Nuclear Technology*; and two others (one published and one in press) in *RadWaste Solutions*, gave two invited presentations to the Nuclear Waste Technical Review Board, five papers at the International High Level Radioactive Waste Management Conference, one paper at Waste Management 2011, and a talk and poster at American Geophysical Union (AGU).

Significance:
This project is aligned with Sandia's energy security mission of enabling a US nuclear enterprise by providing a demonstrably safe way to store nuclear waste. Our work is specifically targeted at making deep borehole disposal a thrust area in DOE-NE (Nuclear Energy) and Sandia the technical lead.

Transportation Energy Pathways
141670

Year 2 of 3
Principal Investigator: G. Barter

Project Purpose:
In the coming decades, personal transportation options and the required infrastructure must undergo a fundamental transformation to achieve the nation's economic, environmental, and national security needs. New fuel sources, stronger consideration of greenhouse gas emissions, and application of new technologies will contribute to this transformation to sustainable transportation solutions. Moreover, the heterogeneous distribution of potential resources and populations suggests that the US should consider regional transportation energy systems rather than monolithic national architectures. The complexities and unintended consequences of such a multipronged approach are not well understood (e.g., how can mixes of energy sources and improved efficiency standards fit together into secure, robust, and sustainable solutions? What technological innovations will be needed?). Systematic, dynamic, integrated analysis methodologies and tools are needed to understand the complex transformation from the current petroleum-based transportation system to one that incorporates alternative fuels and electric vehicles.

This project is developing an energy pathways model (EPM) of regionally deployed transportation systems for a representative set of future transportation-energy sources, technologies, and demands. The EPM will be unique in its comprehensiveness and its ability to analyze the time evolution of technological development across multiple transportation energy systems. By considering the complex interrelationships of potential transportation energy systems, this capability will enable assessments of the synergies and potential of these systems, identification of technological gaps, and compatibility with the current and future vehicle fleet. This project is creating a modular transportation energy pathways analysis methodology that can be continually expanded and improved to provide an enduring capability to answer the transportation energy questions of highest importance to the nation. The EPM will provide a foundational tool for Sandia's transportation energy strategy, will enable Sandia and its partners to assess technology gaps with the highest risks/rewards, and will identify key issues and constraints in transitioning to future transportation energy mixes.

Summary of Accomplishments:
During the past year, we completed a significant milestone on the project: the development of a regionally resolved model that integrates vehicles, energy carriers, and energy supplies. This model incorporates consumer choice between competing vehicle drive trains and breaks vehicles into different size classes, based on feedback from our auto industry partners. The model also includes the dependence of regional recharging/refueling infrastructure development on market penetration of the corresponding vehicle drive trains. The model divides the US into the North American Electric Reliability Council (NERC) Regions, with different energy supply curves, electricity generation mixes, fuels costs and availabilities, vehicle mixes, and consumer choices in each region. We have defined baseline model parameters, and appropriate ranges for these parameters for our sensitivity analyses, based on a review of the literature and in consultation with our UC-Davis and General Motors (GM) partners. We have also sense checked the model and benchmarked model results to other studies.

We have conducted initial analyses — focusing on plug-in hybrid electric vehicle (PHEV) and battery electric vehicle (BEV) market penetration — using this model, with an emphasis on sensitivity of greenhouse gas (GHG) emissions, petroleum use, and PHEV and BEV market penetration to underlying technology and policy assumptions. The model and analysis results have been reviewed by the

UC-Davis Institute for Transportation Studies, Argonne's Energy Systems Division, and by the DOE Energy Efficiency and Renewable Energy's Vehicle Technologies Program. In particular, the Vehicle Technologies Program has expressed interest in our conducting additional analyses using extensions of the EPM model beyond the scope of this project. The model has been updated to reflect feedback from the above interactions and analyses re-run accordingly.

Significance:

America's national security is increasingly dependent on its access to reliable, clean, and affordable energy. The EPM provides a foundational tool for Sandia's transportation energy strategy and will guide future technology assessments by identifying technology gap areas with the highest risks/rewards. For DOE's Office of Energy Efficiency and Renewable Energy, US industry, and others, the capability developed in this project enables exploration of options to enable national transportation infrastructure transformation. The capabilities built through this effort will be global in nature and can be tailored for international analyses, providing Sandia with opportunities to impact global transportation energy development.

Guiding Options for Optimal Biofuels
148066

Year 2 of 3
Principal Investigator: S. M. Paap

Project Purpose:
It is widely recognized that current biomass-derived transportation fuels, especially ethanol, suffer from a number of shortcomings, including incompatibilities with existing vehicles and infrastructure, resource-intensive production methods, and low energy densities. It is also increasingly well recognized that any sustainable biofuels solution will be highly region-dependent due to differing feedstock growth conditions and available infrastructures. A key missing piece in our understanding is how to integrate these sometimes competing considerations across diverse domains that span from agricultural resources and biomass characteristics through conversion processes and combustion properties in order to enable large-scale deployment of biofuels in a responsible manner.

The complex problem of selecting an optimal biomass-derived transportation fuel requires physically relevant yet computationally manageable models that adequately represent the main processes driving the overall system. These components are currently lacking. The proposed project will help close this critical gap by developing simplified models representing the production and composition of biomass feedstocks as well as the conversion of these feedstocks to various fuels. These simplified models will then be incorporated in a multiscale and multidomain model framework that couples the selection and development of feedstocks and conversion processes to provide a basis for exploring the entire pathway from agricultural inputs to the end use of the fuel, while incorporating realistic region-specific constraints such as agricultural conditions, cost, and infrastructure requirements.

The proposed project looks beyond existing technologies and infrastructure in order to probe the fundamental constraints and tradeoffs affecting the deployment of biomass-derived transportation fuels. The real innovation here lies in the multidisciplinary integration across temporal, spatial, and conceptual scales that will result in a unique modeling framework that leverages Sandia's strengths in systems modeling and analysis in a way that informs better decision-making with sparse and/or uncertain data inputs. We seek to ultimately gain valuable insight into what a future biofuels solution could and should look like.

Summary of Accomplishments:
The most significant R&D accomplishments of FY 2011 were the completion and testing of a model representing the biochemical conversion of biomass feedstocks to liquid transportation fuels, and the use of this model to generate publishable results. The model incorporates multiple pathways to convert lignocellulosic material — corn stover, switchgrass, miscanthus, and poplar — to either ethanol or fatty acid ethyl ester (FAEE), comprising independent modules corresponding to the major processing steps: biomass pretreatment, hydrolysis of cellulose and hemicellulose to sugars, fermentation of sugars to fuel, and product recovery and purification. Alternative technology choices are available for the pretreatment step, allowing the analysis of 16 individual pathways from feedstock to fuel. The relevant metrics for the conversion process are net electricity production, water consumption, annual fuel production, and minimum fuel selling price (based on a cash flow analysis). Colleagues within Sandia and at the Joint BioEnergy Institute (JBEI) provided data and subject matter expertise that were leveraged to guide the construction of the model and to select the technical parameter ranges and most likely values that best reflect the current state of technology.

The conversion process model was validated using published data from previous studies of biofuel production processes, and the metrics of interest were evaluated for each combination of feedstock, process configuration, and fuel. A Monte Carlo analysis was conducted in order to gauge the uncertainty in the model predictions, identify the most influential system parameters for each individual pathway, and draw conclusions across the various pathways regarding their relative performance. Because the microbial production of non-ethanol fuels is at an earlier stage of development, the model was also employed to assess the potential impact of future process improvements on the biodiesel pathways relative to those for ethanol. Work has begun on a manuscript for publication incorporating these results.

Significance:

This project directly supports the energy security mission of the DOE and Sandia by developing capabilities that offer insight into the most promising pathways to large-scale deployment of reliable, clean, and affordable biomass-derived transportation fuels. The project enhances the impact of science and technology innovations by identifying high-potential biofuels research areas to more effectively leverage DOE resources in support of this mission. The conversion process model that we have developed offers a way to connect the various biochemical pathways from cellulosic biomass to biofuels via the underlying technical parameters that govern their behavior. Our results challenge widely held assumptions regarding the relative advantages and disadvantages of competing biofuels pathways, in particular highlighting the tradeoffs between ethanol and so-called advanced biofuels. These conclusions are currently being incorporated into a manuscript for publication in a peer-reviewed journal. Our analysis offers concrete paths to process improvement and provides valuable insight to the level of improvement that can be expected in terms of relevant economic and environmental metrics.

We have leveraged connections between Sandia and the DOE's JBEI to ensure that our work reflects state-of-the-art knowledge of advanced technologies being applied to the production of biofuels. Our unique access to expert opinion from subject-matter experts at JBEI has allowed us to create a framework for the analysis of biofuels production that is general and flexible enough to readily incorporate advances in technology across the entire process. Beyond the current project, this modeling framework may be expanded to incorporate new conversion process pathways; it may also be incorporated into larger models and analyses in support of Sandia's energy security mission.

The potential for expanding the application of our conversion process model to related research areas is reflected in a proposal that was submitted to DOE's Office of the Biomass Program (OBP). In this project, we outlined an approach to incorporate additional water-immiscible biofuels – along with the appropriate product recovery technologies – into the model in order to generate a design case for the production of these fuels from cellulosic biomass. Similar opportunities exist to explore alternative biomass pretreatment, cellulose hydrolysis, and sugar fermentation technologies, several of which are being developed either within Sandia or at JBEI.

Our efforts to model the conversion of biomass feedstocks to transportation fuels have also led to a collaboration with the China Automotive Energy Research Center (CAERC) at Tsinghua University in Beijing, China. A visiting researcher from CAERC participated in joint model development efforts during a stay at Sandia; active engagement with the researcher has continued beyond the visit, strengthening Sandia's ties to an important partner and potentially offering opportunities for further collaboration. Our partnership with Tsinghua University in the area of biofuels modeling served as the analysis component of a successful proposal to establish a US-China Clean Energy Research Center (CERC) for Clean Vehicles.

Ground Water and Snow Sensor Based on Directional Detection of Cosmogenic Neutrons
149563

Year 2 of 3
Principal Investigator: R. L. Cooper

Project Purpose:
The impact of water on society is hard to overstate. Water security and management is only possible with advanced models of hydrologic processes. To build an accurate model, experimental observations of soil water, snowpack, and canopy water content are required. These observations serve as direct inputs into a wide array of predictive models: rainfall-runoff modeling, stream flow forecasting, vegetation dynamics, surface and ground water interactions, drought prediction, fire hazard, and weather. This project addresses the scale in water content measurements. At one extreme, hydrologists and geologists can assay water content by direct, invasive probing at length scales of a few centimeters. However, it can be quite expensive to obtain time-dependent data for a large number of locations. At the other end of the spatial scale, there is satellite monitoring, which is sensitive at the level of a hundred kilometers square and can provide long-term monitoring. One concern about the satellite data is that is requires on-the-ground calibrations over an area with a diameter of up to several hundred meters.

In this project, we are developing a fast-neutron detector to measure the cosmic ray neutron flux in order to measure soil moisture. Soil that is saturated with water has an enhanced ability to moderate fast neutrons, removing them from the backscatter spectrum. The detector is a two-element, liquid scintillator detector. The choice of liquid scintillator allows rejection of gamma background contamination from the desired neutron signal. This enhances the ability to reconstruct the energy and direction of a coincident neutron event. The ability to image on an event-by-event basis allows the detector to selectively scan the neutron flux as a function of distance from the detector. Calibrations, simulations, and optimization have been completed to understand the detector response to neutron sources at variable distances and directions. This has been applied to laboratory background measurements in preparation for outdoor field tests.

Summary of Accomplishments:
The detector concept has achieved nearly all the first-year milestones. A working model of the soil response to the cosmic ray neutron spectrum has been completed. There is a strong modulation of the fast-neutron spectrum when modest amounts of water are introduced. The detector is most sensitive to the region where the modulation is greatest (~1-5 MeV).

Using laboratory tests with radioisotopes, a two-element liquid scintillator detector was developed that could effectively reject gamma backgrounds and measure both singles and coincidences of neutron events. Using an AmBe neutron source, the imaging and energy spectroscopy capabilities of the detector have been identified. The detector can identify to at least 30° along the axis of symmetry in an event-by-event method. If the aggregate number of counts causing a coincidence in one direction is compared to the other, the fraction can precisely determine the direction of a single source.

The most important result is the relatively high rate of neutrons available for analysis. This was one of the technical risks to this approach, and it is reasonable to assume that the fast neutron detector can be further optimized.

Significance:

The project aligns with DOE science, energy, and nuclear security missions. The security of the water supply is a foundational element of a comprehensive national security plan. The threat of global climate change is very real, and a complete picture of the climate requires accurate and precise water measurement in all forms (rain, soil water, snowpack, canopy water, etc.). Special nuclear material (SNM) detection will also benefit from this work.

CO_2 Reuse Innovation — Novel Approach to CO_2 Conversion Using an Adduct-Mediated Route
151300

Year 1 of 3
Principal Investigator: R. Kemp

Project Purpose:
The need to convert "useless" carbon dioxide (linear CO_2) into valuable products is of high interest worldwide. Performing this process at as low a temperature as kinetically possible is also advantageous, as it minimizes the energy input into the system as well as lowers the possibility for undesired side reactions. In order to achieve success, it is necessary that Sandia explore multiple routes to CO_2capture and fixation. We have recently prepared complexes that form CO_2 adducts with inexpensive, plentiful main group elements such as tin and zinc. Interestingly, the CO_2 fragments in these metal adducts are now bent significantly from linearity in the solid-state crystal structures. We hypothesize that, given the correct combination of metal and ligand structures, the "bent" CO_2 molecule will be easier to either chemically or electrochemically reduce to organic products. If demonstrated, this would be an important technology for DOE and Sandia. However, improvements in moisture and thermal stability of the various organometallic complexes are required in order to produce organic products. We are examining various valence-active main group metals with low-to-high electron counts to determine which metals most effectively transfer electrons into the CO_2 framework. These electrons can be provided either electrochemically or chemically with appropriate reducing agents. Key within our research plan is an evaluation of the role of each specific reductant. The nature of the metal-ligand interaction (sterics and electronics) is also being studied experimentally and computationally, as understanding the stability of this combination is critical to scientific advancement. Ligands will be synthesized to minimize sensitivity to protic-containing solvents or reagents. From these individual component studies, an entire catalytic system will be designed and chemically constructed to evaluate the hypothesis that chemical or electrochemical reduction of CO_2 can be facilitated by main group metal adduct formation.

Summary of Accomplishments:
During the initial year of this project, we have produced several accomplishments, including setting up the joint project with the two University of Vermont researchers. A research-planning visit was held to coordinate research thrust areas. The initial example of an Sn-CO_2 adduct upon which this project is based was prepared as a low-yield product along with a crystalline byproduct that could be separated only by physical methods. Recently, we have discovered how to make only the desired crystalline Sn-CO_2 adduct with no side products. As well, we have shown conclusively that the CO_2 is a reversibly bound adduct because CO_2 can be forced to leave by gentle heating or by storage. In solution, reactions with labeled $^{13}CO_2$ show exchange at room temperature. Under a CO_2 atmosphere, the adduct is stable indefinitely. This is an excellent result as it shows the CO_2 is bound strongly to the metal, but not so much as to retard the elimination of the eventual product. Initial electrochemical results on the reduction of this compound have been inconclusive. The material is electroactive; however, the ligand backbone may be too fragile to survive the electrochemistry. To rectify this, we have been preparing a number of modified ligand-metal combinations that should provide more stability in the electrochemical environment. We are preparing new ligands for zinc and tin based on amidinates, carbon-bound phenolates, 2,6-diamino- and 2,6-diphosphino-substituted arenes, and modified hydroxyquinolines to overcome this possible deficiency. Metal complexes of these have been made and some have undergone CO_2 testing, although results are not complete yet. As well, we have started a new thrust area in which inexpensive transition metal complexes are used. Three papers have been published that acknowledge

this project, all concerned with CO_2 reactions with Sn complexes that form the basis of the proposed research.

Significance:
Sandia is currently involved in research on splitting CO_2 using high temperature methods and materials to help solve the energy crisis. Additionally, there are other ongoing DOE projects that involve CO_2 capture and sequestration. Our approach combines and complements these ongoing efforts by using a novel and unique approach involving inexpensive, main group metals, and in a new thrust area — inexpensive and earth-abundant transition metal complexes. The significance of our work can be put in context in at least two different levels. At a societal level, in order to minimize climate change there is a tremendous desire to reduce the amount of CO_2 that is emitted into the atmosphere. Alternatively, as the internal combustion engine will clearly be around for decades to come, an alternative is to try to recycle, or re-convert the CO_2 present in the atmosphere into more useful small organic molecules that can be used as fuels or fuel precursors. Our technical approach to prepare more easily reduced complexes of CO_2 fits nicely into this high-level concern of society. On a more fundamental basis, DOE has a great deal of interest in understanding the basic chemical reactions of molecules such as CO_2 that are normally unreactive. Understanding the basic chemical reactions of CO_2 with inexpensive main group elements (such as tin, zinc, or bismuth) or amphoteric earth-abundant transition metal complexes (such as iron, nickel, or cobalt, for example) can provide valuable information for the many scientists working in CO_2 conversion chemistry. We have already submitted three manuscripts on various aspects of CO_2 conversion chemistry based on our work with main group elements. If successful, this low-temperature, low-pressure process using inexpensive and abundant metals will help on the path to energy independence and mitigation of global warming.

Refereed Communications:
C.A. Stewart, D.A. Dickie, B. Moasser, and R.A. Kemp, "Reactions of CO_2 and Related Heteroallenes with CF_3-Substituted Aromatic Silylamines of Tin," *Polyhedron*, June 2011.

C.A. Stewart, D.A. Dickie, Y. Tang, and R.A. Kemp, "Insertion Reactions of CO_2, OCS, and CS_2 into the Sn–N Bonds of $(Me_2N)_2Sn$: NMR and X-ray Structural Characterization of the Products," *Inorganica Chimica Acta*, vol. 376, pp. 73-79, 2011.

D.A. Dickie, E.N. Coker, and R.A. Kemp, "Formation of a Reversible, Intramolecular Main-Group Metal-CO_2 Adduct," *Inorganic Chemistry*, vol. 50, pp. 11288-11290, November 2011.

Development of Alkaline Fuel Cells
151301

Year 1 of 3
Principal Investigator: M. Hibbs

Project Purpose:
We propose to develop alkaline anion exchange membrane (AAEM) fuel cell technology to a point of proof of feasibility for portable power applications. This technology has the potential to revolutionize fuel cell use in portable power applications. Alkaline fuel cells without precious metal catalysts were developed years ago but these traditional alkaline fuel cells required a liquid electrolyte because they lacked a true AAEM and suffered from reliability problems because of the formation of solid carbonate in the presence of CO_2. Current research on AAEM fuel cells (AAEMFCs) has shown that these membrane-based systems will not generate solid carbonate due to the absence of any mobile cation. They also mitigate potential corrosion problems by removing the liquid electrolyte. Research in this area has been limited, however, and the power densities of AAEMFCs lag behind those of their proton exchange membrane (PEM) counterparts. A major contributor to the low power densities is poor reactant mass transport in the electrodes and this, in turn, is due largely to the lack of available ionomers to use as binders in the electrodes. The challenge for this project is to demonstrate a methanol AAEMFC with a maximum power density comparable to that of a methanol PEM fuel cell that does not utilize any precious metal catalyst.

Mass transport within the electrodes is critical to performance and yet, no electrode architecture has been specifically tailored and optimized for use in an AAEMFC. Because Sandia has developed cationic polymers for AAEMs that can also be dissolved in solvents such as alcohols, we are in a unique position to work with catalyst developers to experiment with the design of electrodes for AAEMFCs. This field is still in its infancy (compared to PEM fuel cell electrode design).

Summary of Accomplishments:
One of the stated goals of this project is to attach alternative cationic groups such as guanidinium to the highly stable poly(phenylene) (PPh) backbone previously used for Sandia's anion-exchange membranes (AEMs). During year one, poly(sulfone) (PS) and PPh-based membranes with benzylquanidinium (BG) cations were both synthesized. Conversion of these membranes to hydroxide form revealed an unexpected change in properties that nuclear magnetic resonance spectroscopy showed to be due to degradation of the BG groups after nucleophilic attack by hydroxide ions at the benzylic position on both polymers. Elucidation of this degradation mechanism led to a new cation design.

Mechanical testing of both PS and PPh-based AEMs after treatment with sodium hydroxide solutions at varying conditions was performed and indicated that the PPh membranes are much more stable than PS and that the PS membranes may be unsuitable for AEMs. This is a critical result as many other groups doing AEM research are using PS-based membranes and it will require further verification of molecular weight changes prior to publication.

Another goal of this project is to improve fuel cell performance by facilitating the transport of fuel (methanol) within the electrodes. Part of this issue will be addressed by altering the structure of the AEM polymer to render it more permeable to methanol. To this end, two new PPh monomers have been synthesized. These monomers will incorporate short ethylene oxide units into the backbone to increase polymer flexibility and, hence, permeability. Measurement of methanol diffusion coefficients by solid-state nuclear magnetic resonance (NMR) has been done for baseline AEMs and will be performed on the new PPh materials as they become available. Additionally, the transport issue will be addressed during membrane electrode assembly fabrication research at the Colorado School of Mines. Electrochemical evaluation of templated non-precious metal catalysts with baseline PS and PPh ionomers is under way at the University of New Mexico.

Significance:
One of the goals of the DOE Office of Energy Efficiency and Renewable Energy is to bring clean, reliable and affordable energy technologies to the marketplace. Specifically, the mission of the DOE Fuel Cell Technologies Program is to enable the widespread commercialization of fuel cells in diverse sectors of the economy. This project would support that mission by demonstrating an AAEM fuel cell that can achieve increased power densities without using a precious metal catalyst. The resulting reduction in the cost of the energy produced will make development of AAEM fuel cells more attractive to fuel cell manufacturers.

Our findings are significant because they show that the most commonly used polymer for AEM research (polysulfone) is not a viable option due to its lack of chemical stability under high pH conditions. AEM research will need to shift to more durable polymers that tend to also be more difficult to functionalize. Since we already have an AEM based on a more durable polymer (polyphenylene), Sandia is in a good position to lead research in this area and/or attract research partners.

Constitutive Framework for Simulating Coupled Clay/Shale Multiphysics
151302

Year 1 of 3
Principal Investigator: F. D. Hansen

Project Purpose:
Clay and tight shale geologic formations are increasingly promising as host media or engineered barrier materials for nuclear waste disposal, unconventional gas resources, and as caprocks for CO_2 sequestration. Clay minerals and formations are known for compositional and structural variability. Although much effort has been directed toward understanding behaviors of clay/shale media, significant technical gaps still exist. For example, existing geochemical and geomechanical studies have been performed for a limited set of clay materials, and there is no systematic framework for modeling important aspects of system performance across the full spectrum of applications. For nuclear waste disposal, such a framework would include a set of constitutive relationships based on mechanistic understanding of relevant physical and chemical processes, and should capture the variability in clay characteristics (e.g., mineral type, pore size, and pore connectivity) and its impacts on radionuclide transport. Many of these constitutive relationships have not been developed or validated.

We are engaged in two research areas that target behaviors of clay media that make them desirable for these applications. We are first establishing a general functional dependence for radionuclide sorption/retardation on the chemical compositions, mineral structures, and formation factors (e.g., porosity and pore connectivity) for clay/shale media, based on a systematic experimental and modeling study of a representative set of clay materials. We will then describe constitutive geomechanical (e.g., clay mineral swelling, compaction and clay formation creep/damage) and transport (e.g., permeability and diffusion coefficients) properties as functions of waste disposal conditions (e.g., temperature and water chemistry). The developed constitutive relationships will be incorporated into the Sierra Mechanics codes for simulating multiphase, multicomponent, and nonisothermal reactive transport, coupled to nonlinear geomechanics in clay/shale media. The research will produce and validate an innovative and general modeling framework that can be applied to a wide range of national and international issues.

Summary of Accomplishments:
On radionuclide sorption physics, our results support the original hypothesis that sorption properties of clay minerals can potentially be systematized in terms of mineral composition and structure. Seven pure clay minerals and two field samples from Wyoming bentonite and Callovo-Oxfordian formation in France were obtained and characterized using x-ray diffraction (XRD), Brunauer, Emmett, and Teller method (BET), and surface titrations. A total of ~ 200 surface titrations have been completed for clay minerals. Experiments have been performed for Ni and iodine sorption onto various clay mineral phases. Experimental data have clearly indicated the heterogeneous nature of sorption sites on clay minerals and demonstrated the feasibility of using titration data to deconvolute this heterogeneity. Based on iodine sorption data, we discovered a new sorption mechanism that, if confirmed, will open a new avenue for designing adsorbent materials. We have also discovered a new set of high-performance materials for iodine sorption. One patent application is filed. In our modeling effort, we have formulated a mathematical model for coupling thermal-hydrologic-mechanical-chemical (THMC) processes in clay formations. Code development has been initiated for inclusion of an elasto-cap plasticity model for partially saturated clay materials into Sierra. A memorandum of understanding (MOU) has been obtained with ANDRA (The French National Agency for Radioactive Waste Management) that allows

us to obtain data from French underground tests as validation/verification for the Sierra Mechanics simulations. We are consulting with Texas A&M University to integrate double structured plasticity model to allow for coupled suction, dry-out, and swelling and their effects on radionuclide sorption and transport in clay materials. We attended the ANDRA meeting at Chatenay, France on underground THM tests. We chaired oral and poster sessions on "Coupled Mudstone Multiphysics" and gave two invited lectures on clays at the American Geophysical Union (AGU) Fall meeting.

Significance:
The proposed research will significantly advance DOE's capabilities for siting and analyzing performance of facilities in clay or shale formations. Sorption is one of the key properties, along with low permeability and chemically reducing conditions, that retards radionuclide migration in such media. The proposed sorption research will support a systematic approach to predicting sorption in various geologic settings. Similarly, an advanced constitutive modeling approach will bridge the gaps between modeling and experimental results reported by different investigators, for responses to CO_2 injection, excavation, and heating. This advancement increases confidence in performance predictions of these vital national missions.

Refereed Communications:
Y. Wang, H. Gao, and H. Xu, "Nanogeochemistry: Nanostructures and their Reactivity in Natural Systems," *Frontiers in Geochemistry,* A. Parker and H. Russell, eds., Wiley-Blackwell, pp. 200-220, 2011.

Y. Wang, H. Gao, A. Miller, and P. Pohl, "A New Generation of Adsorbent Materials for Entrapping and Immobilizing Highly Mobile Radionuclides," *Waste Disposal, InTech,* X.-Y. Yu, ed., 2011.

In-Situ Diagnostics for Fuels Model Validation with ACRR
151303

Year 1 of 3
Principal Investigator: E. J. Parma, Jr.

Project Purpose:
In past transient irradiation studies of fuels, there has been no reliable way to get meaningful data on physical changes during the pulse. Past Sandia studies have only gathered qualitative information about fuel form changes by taking videos during the transient events, and French researchers have measured only axial expansion in situ; fuel rods typically fail due to radial strain. Data on radial strain has only been obtained during post-irradiations examinations, which occur months after irradiation and at lower temperatures than at irradiation. While this information is valuable, there has been no way to gather quantitative transient data in situ during irradiation that can directly validate fuels models.

The detailed measurement of in situ fuel clad strains during a reactor transient has never been accomplished. This project will develop and verify experimental techniques and procedures to obtain these data and apply the techniques to fuel pins in a safe manner. This will represent a new and unique capability for the world's nuclear research community. The project is limited to the development of new experimental procedures and the verification of them using both non-fueled and fueled test samples. Results from the Sandia-developed MPALE (Material Point Automated Lagrangian Eulerian) code will be compared with these new data.

There are two primary advancements that will need to be made to the Digital Image Correlation (DIC) technique in order to make the desired measurements. The first will be to use DIC with a borescope. This will represent an incremental advance that will require the implementation of nonlinear image distortion correction in DIC. This has already been implemented for use with stereomicroscopes and should be able to be modified for use with the borescope-imaging configuration. The more challenging advancement will be in the area of creating an appropriate speckle pattern that survives the high heat loads that will be encountered in the experiment, while maintaining the pattern for correlation in DIC.

Summary of Accomplishments:
A test assembly for annular core research reactor (ACRR) central cavity testing has been designed, fabricated, and assembled. The assembly was built to meet the size, material, and other constraints of the ACRR. The assembly is flexible and can be reconfigured for different experiments as needed for the different measurement techniques that will be used. A pressure test assembly for measuring strain in the laboratory has been designed, fabricated, assembled, and tested. The assembly was built to allow for pressure testing of up to 1500 psi to produce stain in pressure tubes. The rig includes all of the pressure hardware and data acquisition hardware and software.

Initial digital imaging correlation measurements have been made on stainless steel pressure tubes that simulate cladding strain in nuclear fuel pins. Different pressures and temperatures have been tested to determine the lower limit on strain that can be measured and the effects of temperature on the measurements.

High temperature strain gauges have been purchased, assembled, and tested on stainless steel pressure tubes. Different pressures and temperatures have been tested to determine the lower limit on strain that can be measured and the effects of temperature on the measurements. A dry run test will be performed of the test rig and strain hardware in the ACRR central cavity. The purpose of the test will be to determine noise and other effects on the strain measurements associated with the in situ conditions of the reactor.

Significance:

As new reactor systems are being investigated, each brings with it new fuels challenges for designers and regulators. Each of these fuels will require extensive modeling and testing, including a set of transient tests. The ACRR is the only existing US reactor capable of performing these transient tests, but it has not been used for fuels tests in over a decade. Reestablishing this capability, especially with a new set of tools that will complement the modeling effort, will provide the DOE complex with a needed tool. Potential customers include DOE, the Nuclear Regulatory Commission, commercial vendors, and international partners.

Tier 2 Development of Sandia's Air Bearing Heat Exchanger Technology
151304

Year 1 of 3
Principal Investigator: J. P. Koplow

Project Purpose:
In a prior project, we obtained breakthrough results in a proof-of-concept demonstration of the "air bearing heat exchanger." This work was unusual in that it represented a fundamental new approach to a very old problem of great importance in the energy sector that appeared to have been studied exhaustively. A relatively high level of risk was regarded as worth the investment in this exploratory work because of the large potential payoff in real-world applications. Having successfully demonstrated the proposed mechanism for solid-gas heat transfer in the laboratory, we are now working to mature this new technology and prove its practicality for real-world applications. The first requirement for technology maturation is a comprehensive effort in turbo-machinery fluid dynamic modeling; a complete understanding of device physics is required to determine device scaling laws, optimization, and performance trade space. Technology maturation also requires several elements of further innovation (such as development hydrodynamic gas bearing technology compatible with the other requirements of this application) to enable widespread adoption of this technology in real-world applications.

The air bearing heat exchanger represents a fundamental new technology in the field of heat transfer. This radically new device architecture overcomes the longstanding problem of thermal boundary effects by placing the heat exchanger boundary layer in an accelerating (rapidly rotating) frame of reference. This new device architecture can simultaneously provide reduced noise and/or electrical power consumption, and completely solves the problem of heat sink fouling (which is otherwise inevitable in real-world applications). Our ultimate goal is to have air bearing heat exchanger technology penetrate a wide variety of applications in the energy sector so as to substantially reduce average and peak loading of the electrical grid.

Summary of Accomplishments:
Accomplishments to date include the following: 1) design and fabrication of version 3 prototype radial-flow air bearing heat exchanger, 2) design and fabrication of direct-drive 10-krpm heat-sink-impeller test bed, 3) design and fabrication of customized 150-W polyimide film heater assembly, 4) development and testing of cold forging approach to monolithic device fabrication in conjunction with Cooliance, Inc., 5) development of centrifugal pre-compensation fabrication scheme in conjunction with Cooliance, Inc., 6) measurement of hydrodynamic air bearing parameters (gap distance as a function of rpm and downward magnetic restoring force, and heat transfer as a function of angular velocity), 7) invention of the axial-flow device architecture to solve the fin internal heat transfer problem, 8) invention of the planar particle source imaging technique, 9) development of non-air-bearing device architectures for thermal management of light-emitting diode (LED) lighting systems, 10) design and fabrication of integrated-heat-pipe base plate assembly for version 3 device, 11) design and fabrication of non-heat-pipe base plate (so as to allow quantitative determination of heat pipe performance), 12) preparation and filing of provisional patent application for Rotary Cooled Solid State Lighting (RCSSL), and 13) preparation and filing of provisional patent application for Axial Flow Air Bearing Heat Exchanger. We have also set up collaboration with General Electric Global Research for advanced computational fluid dynamics (CFD) modeling. We are now assembling and troubleshooting version 4 prototype. Preparation for "Industry Day" is also in progress.

Significance:

The proposed work is directly relevant to DOE's mission in that a breakthrough in air-cooling technology could provide an estimated 7.5% reduction in total US electrical power consumption; by comparison, the total amount of electricity generated by all alternative energy sources combined is currently 3.0%. Cooling loads are also the main culprit with regard to electricity demand load spikes, which have a direct bearing on grid surety, operating margin, and requirements for installed generating capacity. Air Bearing Heat Exchanger technology is also well suited to address increasing concerns about loading of the electrical grid associated with the expanding information technology (IT) sector.

Fundamental Study of CO_2-H_2O-Mineral Interactions for Carbon Sequestration, with Emphasis on the Nature of the Supercritical Fluid-Mineral Interface
151305

Year 1 of 3
Principal Investigator: C. R. Bryan

Project Purpose:
Carbon sequestration via underground storage in geologic formations is a proposed approach for reducing industrial CO_2 emissions. There is a direct need by operators/regulators for better, informed models that incorporate coupled multiphysics processes arising from subsurface CO_2 injection and storage. However, current models do not consider processes at the supercritical CO_2 ($scCO_2$)-mineral interface and their potential effects on long-term subsurface CO_2 storage. Interfacial processes control the wetting properties of minerals and the chemical reactivity at the $scCO_2$-mineral interface. The interface properties will be strongly dependent upon the activity of water in the supercritical fluid, which will change as initially anhydrous $scCO_2$ absorbs water from formation brine. As $scCO_2$ water activity increases, the water layer on hydrophilic mineral surfaces will thicken, with concomitant changes in surface properties that will affect how $scCO_2$ wets mineral surfaces, reservoir/caprock hydrological properties, and the mobility of $scCO_2$. Capillary condensation of water from $scCO_2$ and coalescence of water films may also occur. Moreover, the development of a water layer may be critical to mineral dissolution reactions in $scCO_2$, and may affect attractive forces between clay particles. Data are currently lacking to incorporate these processes into models for CO_2 sequestration.

We are developing key theoretical, experimental, and modeling capabilities for understanding the interactions of supercritical CO_2-H2O fluids with geologic formations. Inherent technical challenges exist in performing nanoscale studies of the $scCO_2$ -mineral interface, and in upscaling nano/core-scale results to reservoir-scale processes. We use innovative high-pressure spectroscopic methods to evaluate the $scCO_2$ -mineral interface, and will develop methods for evaluating formation of surface water films in $scCO_2$ and their effect on rock hydrologic properties. This research will provide improved constitutive models and needed experimental data for evaluating and validating the long-term performance of subsurface CO_2 storage.

Summary of Accomplishments:
1. Development of the capability to perform experimental work evaluating geochemical and hydrologic processes in supercritical CO_2. Sandia has not previously had this capability.
2. Experimental work has been initiated, although delivery of several custom-built pieces of pressure equipment was slow. Delivery of one critical piece, the Fourier transform infrared spectroscopy attenuated total reflectance (FTIR-ATR) cell, has been delayed until November 2011. To mitigate this, an alternative, unique approach has been pursued for FY 2011, evaluating quartz crystal microbalance techniques for direct measurement of water film adsorption from $scCO_2$.
3. Models for fluid-mineral interface processes in supercritical CO_2 are being developed. Three articles are in progress that will be published in refereed journals; a draft of the first has been completed.
4. Three abstracts on modeling and experimental work were accepted to the December 2011 American Geophysical Union (AGU) meeting. The team members will co-chair a two-part session at the meeting.

5. We have leveraged the work by submitting two companion proposals for beam time at the Los Alamos Neutron Science Center (LANSCE) neutron beam facility, to evaluate clay swelling in scCO_2. Both have been funded.

The model development efforts address three areas. First, a thermodynamically based model for water adsorption and capillary condensation is being developed. This model, which is derived from vadose zone models, estimates adsorbed water film thicknesses and properties by calculating disjoining pressures, accounting for van der Waals, electrostatic, and structural forces. Capillarity is captured using an augmented Young-Laplace equation, utilizing the adsorbed film thickness to adjust the radius of curvature when evaluating capillary forces for realistic pore geometries. Two other models, for residual trapping of scCO_2 as a function of effective surface tension and CO_2 injection rate, and for mineral precipitation due to the combined effects of capillary forces osmolality on water transport in scCO_2, are in progress.

Significance:

The proposed work focuses on closing the carbon cycle, one of the highest priorities facing the nation today. This research will provide key constitutive models and experimental data for evaluating and validating the long-term performance of subsurface CO_2 storage. The work may also lead to the development of new technologies (e.g., engineered capillary entrapment) for CO_2 management. By enhancing technical capabilities to effectively evaluate CO_2 sequestration in underground reservoirs, this work supports DOE missions to improve energy security and to respond to global warming/climate change concerns while providing resource management and environmental stewardship. Moreover, the experimental data generated by this project will allow calibration and validation of molecular dynamics models for surface processes, being developed by other CO_2 sequestration projects at Sandia with whom we are collaborating.

Development and Deployment of a Field Instrument for Measurements of Black Carbon Aerosols
151307

Year 1 of 3
Principal Investigator: H. A. Michelsen

Project Purpose:
Atmospheric black carbon (BC) consists of combustion-generated soot incorporated into atmospheric aerosols. BC particles strongly absorb solar radiation and the resulting global warming and regional climate effects are substantial. Brown carbon (BrC) particles are predominantly composed of semi-volatile combustion byproducts and are also suspected of having similar climate effects. In the Arctic, soot settles on snow, decreasing its albedo and leading to melting and further warming. Additionally, aerosols influence cloud properties, leading to large uncertainties in climate models. The physical characteristics of atmospheric particles and the magnitude of their climate effects depend on where they originate, how they mix in the atmosphere, and how their properties evolve as they age. Developing a better understanding of, and parameterizations for, these processes will narrow the uncertainties in climate models. Furthermore, because their physical characteristics depend on their origins and histories, the composition and partitioning among aerosol types can be used as tracers to attribute sources of greenhouse gases (GHGs) for climate treaty verification. BC and BrC particles are small and highly variable in composition and structure, however, and existing instruments are incapable of characterizing them with sufficient sensitivity, specificity, and time response to classify populations of particles in air masses. Aerosol mass spectrometers can speciate particles with sufficient sensitivity but do not provide optical information. Filter techniques are too slow. Current optical techniques provide optical parameters but lack specificity.

We will address the current need for atmospheric inventories of light-absorbing (BC and BrC) organic aerosols and their optical and chemical characteristics by developing a technique and building and deploying an instrument for such measurements. This project is based on a novel combination of experimental and analytical approaches, and both the instrument development and the instrument deployment and analysis of results are in the proof-of-principle phase.

Summary of Accomplishments:
We have designed the multipass (Herriott) cell and collection optics for the field-compatible laser-induced incandescence (LII) instrument and have fabricated the cell mirrors. We have assembled a co-flow diffusion burner, which generates carbonaceous soot (with a carbon:hydrogen ratio of ~8) from ethylene and air, and an ethylene/air premixed laminar burner, which generates soot with more hydrocarbon and less graphitic content for testing our full system. Using soot produced from both burners, we have collected transmission electron microscope (TEM) images and single-pass LII signal with a laser beam from an Nd:YAG laser in the configuration we plan to use in the field instrument. The LII results are consistent with predictions for hydrocarbon-coated (premixed) and uncoated (co-flow) soot. The TEM images demonstrate fractal morphologies for soot sampled from the co-flow diffusion burner, consistent with mature soot containing aggregates of mostly graphitic primary particles. TEM images for soot sampled from the premixed burner demonstrate more globular morphologies, consistent with studies that have linked such material to particles containing significant quantities of aliphatic and polycyclic aromatic hydrocarbons. Particles sampled from the premixed flame were size selected using a differential mobility analyzer (DMA) and captured on TEM grids. Statistical analyses of the resulting TEM images are consistent with size distributions measured with a scanning mobility particle sizer and demonstrate bimodal distributions with a minor second mode from doubly charged particles that passed

through the DMA. The peak of the lognormal distribution of the geometric mean diameter is 91 nm for particles selected with 100-nm mobility diameter, 134 nm with 150-nm mobility diameter, and 156 nm with 175-nm mobility diameter. In addition, we have configured a tunable ultraviolet (UV) laser source using a Nd:YAG laser (1064 nm, 532 nm), dye laser (550-820 nm), and doubling (275-410 nm) and tripling crystals (198-273 nm) to measure UV laser induced fluorescence (LIF) of volatile species.

Significance:
Climate change has been identified as a priority national security concern. DOE has initiated significant expansion of its climate prediction mission to support national strategic decisions that will require expanded datasets and validation. A NASA/DOE/NOAA (National Oceanic and Atmospheric Administration) alliance is attempting to develop a Greenhouse Gas Information System program to support treaty verification. This project will facilitate continuous, widespread measurements of climatologically significant particles, yield parameterizations for regional climate predictions, and provide key tracer measurements for source attribution and treaty verification.

Tailoring Next-Generation Biofuels and their Combustion in Next-Generation Engines
151308

Year 1 of 3
Principal Investigator: C. A. Taatjes

Project Purpose:
Increasing energy costs, the dependence on foreign oil supplies, and environmental concerns have emphasized the need to produce sustainable renewable fuels and chemicals. Domestically produced biofuels for the transportation sector will be key to meeting national goals for energy security and climate-change mitigation. The strategy for producing next-generation biofuels must include efficient processes for biomass conversion to liquid fuels and the fuels must be compatible with current and future engines. New clean and efficient combustion strategies that rely on compression ignition are sensitive to changes in fuel chemistry. Nevertheless, biofuel development generally takes place without any consideration of combustion characteristics, and combustion scientists typically measure biofuels properties without any feedback to the production design. We seek to optimize the fuel/engine system by bringing combustion performance, specifically for advanced next-generation engines, into the development of novel biosynthetic fuel pathways.

We propose an innovative coupling of combustion chemistry, from fundamentals to engine measurements, to the optimization of fuel production using metabolic engineering. We will develop and engineer a new platform for drop-in fuel production from lignocellulosic biomass, using the endophytic fungi, and concurrently generate and exploit a combustion chemistry knowledge base to tailor the biosynthesis. Current biofuels production from lignocellulosic material starts with pretreatment and enzymatic hydrolysis to obtain monomeric sugars, which are then fermented. Our new biosynthetic approach will avoid these two costly steps by using a consolidated process that directly breaks down lignocellulosic biomass by extracellular hydrolytic enzymes and produces an infrastructure-compatible biofuel by fermenting the liberated monomeric sugars. We will investigate the fuel's performance in clean high-efficiency advanced engines and construct predictive combustion chemistry models to guide the optimization towards high-performance compounds. This project will establish, for the first time, the necessary connections among the fundamental chemistry, engine science, and synthetic biology for fuel production, building a powerful framework for codevelopment of engines and biofuels.

Summary of Accomplishments:
We have successfully cultured all target fungi on three biomass feedstocks (corn stover, switchgrass and Eucalyptus) and profiled their volatile organic compound (VOC) products. Cycloalkane/cycloalkene-type compounds, terpene/sesquiterpene derivatives, and long-chain ketones are the predominant identified compounds, all potentially useful fuel molecules. CI-4A produces longer chain hydrocarbons (C14-C18) suitable for diesel combustion. We also demonstrated fungal growth in liquid using plant biomass as the sole carbon source and observed enhance growth rates and VOC production. High molecular weight DNA and RNA was isolated from all four of the endophytes sequenced at the Joint Genome Institute (JGI) and is currently in the JGI assembly and annotation pipeline. This data will facilitate genome annotation and help identify pathways responsible for VOC production, necessary for the optimization of biofuel yields.

We characterized the initial oxidation chemistry of two important classes of fungal biofuels: ketones and cyclic ethers. We developed a set of rate rules for the chemistry of ketone autoignition and validated them against new rapid-compression machine ignition data for a representative molecule, diisopropyl ketone. Engine tests now under way will test the full chemistry model.

Significance:

The predictive simulation of engine combustion, particularly in an evolving fuel environment, is a key part of the DOE mission for improving automobile fuel efficiency. Increased fuel efficiency and the increasing implementation of biofuels derived from renewable feedstocks tailored for the transportation sector are critical elements in the pursuit of national energy security and climate change goals related to reducing dependence on foreign petroleum and limiting greenhouse gas emissions.

Simulation of Component Transport and Segregation in Nuclear Fuels
151310

Year 1 of 3
Principal Investigator: V. Tikare

Project Purpose:
The formation, transport, and segregation of varied components in nuclear fuels fundamentally control their behavior, performance, longevity, and safety. Most nuclear fuels enter service with a uniform composition consisting of a single phase with a small number of chemical components, typically two to three. Often these will segregate in large temperature gradients such as that seen in nuclear fuels. Many different fission products also form and introduce more components into the fuel. The distribution of the components is largely what governs engineering performance and lifetime of nuclear fuels. Further complicating transport of the components is the fact that the fuel has an underlying microstructure consisting of grains, pores, bubbles and more, which is evolving under large temperature gradients during operation. As they evolve, components and microstructural features interact so that composition affects microstructure and vice versa. The ability to predict the interdependent compositional and microstructural evolution in 3D as a function of burn-up would greatly improve the ability to design safe and long-lived nuclear fuels.

We are developing models to simulate coupled evolution of composition and microstructure. Current fuel performance codes address engineering performance by empirically modeling thermal conductivity, fission gas release, strain due to swelling, etc. They do not concern themselves with the underlying compositional and microstructural changes that cause these phenomena. Thus, their predictive ability is limited. Current materials models can simulate complex microstructural evolution processes with limited compositional evolution, but coupling the two is limited and restricted to simple systems. We propose to develop a hybrid model using two models used extensively by computational materials scientists to enable this new capability to simulate coupled compositional-microstructural evolution problems. The hybrid model will combine statistical mechanical methods with continuum thermodynamics to simulate complex processes seen in nuclear fuels thus, making possible predictive capability.

Summary of Accomplishments:
We have successfully combined the Potts kinetic Monte Carlo model with the phase-field model to create a new hybrid Potts–phase-field model. This new model can simulate the evolution of microstructure coupled with chemical and compositional changes that are active in many nuclear materials. This model was demonstrated by studying the evolution in a two-component, two-phase system that forms a simple eutectic. Grain growth and diffusion were coupled. The interfaces between grains and phases are formed by the tradition Potts discrete grain boundary. The same interface when it is a phase boundary is characterized by a diffuse interface that is seen in the phase-field model. Together, this discrete boundary and diffuse chemical gradient boundary define the inter-phase boundaries in this coupled system. While the driving force for coarsening in this coupled system remained the same, reduction in the total interfacial free energy, grain growth kinetics was found to have different kinetics than that of a single-phase system. Grains could only grow as fast as the diffusion would allow the phase boundaries to move. This pinning by the coarsening phase boundaries yielded a grain growth exponent of $n = 3$, rather than the curvature-driven grain growth on $n = 2$. In addition, a model for nucleation of new grains was also investigated. Various nucleation energy criterion and rates were investigated for a system where energy accumulates in the crystal lattice structure as defects due to irradiation accumulate in the grain structure. The nucleation criterion was investigated by simulation recrystallization and dynamic recrystallization. A hybrid Potts – Cellular Automaton (CA) model was

found to given the best results with the correct kinetics for site-saturated nucleation. This was then extended to dynamic recrystallization with a nucleation that was proportional to the local defection energy accumulation.

Significance:

Many technological areas of interest to the DOE will benefit from successful development of this materials model. Any weapons components that are joined by welding or soldering, electronics or microelectromechanical systems (MEMS) devices packaged or embedded in ceramics, and compositional graded specialty materials would benefit from this type of modeling capability. Coupled microstructural-compositional models will also be useful for many fabrication processes such as joining, heterogeneous sintering, electrodeposition and solidification used extensively in weapons components fabrication. The nonproliferation community will benefit because these models can provide detailed description of chemistry, isotopes, and their distribution in a variety of nuclear fuels.

The successful demonstration of a coupled microstructural evolution with chemical evolution with a newly developed hybrid Potts–phase-field model is an important advance in mesoscale modeling of materials. Many materials experience a variety of change in chemical constituent distribution during fabrication or service from very mundane materials like Pb-Sn solders to esoteric nuclear materials like Tristructural-isotropic (TRISO) particulate fuels. This hybrid model enables the simulation of many such processes, especially in nuclear materials that experience changes in chemistry, either due to decay or fission with service. Additionally, the ability to nucleate new features will be a novel capability to the hybrid model as the phase-field model cannot simulate nucleation directly.

This hybrid model capability will be widely applicable to many applications across a number of different materials technologies and customers. Everything from multilayered fuel cells and traditional joints in the nuclear weapons stockpile to nuclear materials will benefit.

Development of a Modeling Framework for Infrastructures in Multi-Hazard Environments
151313

Year 1 of 3
Principal Investigator: D. A. Jones

Project Purpose:
The continuous operation of infrastructure systems is critical to societal welfare. Currently, much of the protection planning against natural hazards and terrorism is done separately for each infrastructure and each hazard. With limited funding, it is important to balance expenditures for terrorism and natural hazards based on potential impacts.

The key S&T problem is creating a modeling framework for investment planning in interdependent infrastructures focused on multiple hazards risks, including terrorism. To develop this modeling framework, three modeling elements must be integrated: 1) sophisticated modeling of natural hazards and terrorism; for natural hazards, this includes the ability to specify a number of events (as well as their probabilities of occurrence) that are consistent with the regional hazards, 2) sophisticated modeling of the terrorists' goals and actions; his representation should admit a range of assumptions about what the terrorist knows and how they identify what to target, given their resource limitations, and 3) sophisticated models of interdependent infrastructures are needed in order to predict the impact of specific terrorist attacks and natural hazard events, as well as how the performance of these systems would change based on investments. The tools developed herein will be applicable across a wide range of infrastructures (DHS, DoD), although we are initially focusing on electric power and its connections to transportation. We will also explicitly identify and illustrate methods to validate each element of the framework.

The success of this project rests on our ability to effectively integrate investment planning with game theory. Since natural hazards do not involve a malicious adversary, the modeling in that area does not have the same complexity (though it is critically important). Global optimization techniques and (non-zero sum) leader-follower assumptions will be used to produce a tractable formulation.

Summary of Accomplishments:
In FY 2011, the focus of the project has been on the modeling of an infrastructure under one threat. Because the goal of the project is to model multiple infrastructures under multiple threats, we have developed a representation for two infrastructures (highway network for Shelby County, TN in the New Madrid Seismic Zone (NMSZ) and the electric power system in the Eastern Interconnection). For both of these systems, we intend to address the threats posed by earthquakes; hence, we have conducted a detailed analysis to identify a suite of earthquake events that represents the earthquake hazard in the NMSZ. We have also developed an optimization model to translate each of these events into a collection of consequence scenarios for both the highway system and the Eastern Interconnection where each consequence scenario gives the damage state for each component in the system. These consequence scenarios are necessary to assess system level impacts from earthquake events. For the electric power system, post-event impacts are modeled using a direct current (DC) flow economic dispatch model. The impacts on the highway system require the use of a dynamic traffic assignment model (DTA). Because our ultimate goal is the development of an optimization framework, the DTA model used must be very fast; hence, we have developed a new algorithm.

We have begun to model terrorism as a hazard to these systems. We have used the Institute of Electrical and Electronics Engineers one-area RTS-96 test network to develop an understanding of how to describe how a terrorist could configure an attack (focus on components that carry the maximum flow, components with the greatest capacity, components that create the greatest impact, etc.). We have also created an initial investment model to consider investments in this system. These efforts have resulted in two publications in review and two others in preparation.

Significance:
DOE's and DHS's missions are to advance the security of the US through technical means including energy and infrastructure security, respectively. These tools can be applied to support these missions. Further, two key responsibilities of the DHS are to analyze and mitigate the consequences of national disasters and terrorist events. This research directly addresses these concerns by creating modeling tools to support investment planning in infrastructure systems that are critical to societal welfare from a multihazard perspective.

Refereed Communications:
A. Li, L. Nozick, R. Davidson, V. Dixit, B. Wolshon, N. Brown, and D. Jones, "A Computationally Efficient Dynamic Traffic Assignment Algorithm," to be published in *Transportation Research Part C*.

N. Brown, J. Gearhart, D. Jones, L. Nozick, N. Romera, and N. Xu, "Scenario Selection for Loss Estimation in Transportation Networks Using Optimization," to be published in *Earthquake Spectra*.

Energy Security Assessment Tools
151314

Year 1 of 3
Principal Investigator: E. D. Vugrin

Project Purpose:
Energy systems serve a keystone role, as other national critical infrastructure and key resource (CIKR) systems depend on them. Disruptions to this sector can affect civilian and military operations, so energy security assessment methodologies must consider this dependence. Current vulnerability assessment (VA) tools are limited in their ability to evaluate the role of energy security. They focus on the identification of vulnerabilities that are "within the perimeter" and may miss dependencies on civilian CIKRs and cyber components. These methods tend to be asset focused, missing mission dependencies and redundancies. Also, they generally address only protection and do not consider recovery actions. Comprehensive energy security assessment tools must be developed to address these limitations. We are developing the capability to evaluate energy security of military missions through the design of quantitative resilience metrics and systematic characterization of mission dependencies. The capability will enable the evaluation of energy security, provide recommendations for resilience enhancing improvements, and enable cost/benefit analysis of improvement options.

This project will advance the current state of mission assessment tools. Including dependencies on civilian CIKRs will enable the incorporation of novel design basis threats (DBTs), resulting in identification of new vulnerabilities. Identification of connections between missions across the military complex will enable application of enterprise-wide solutions for increasing mission assurance (rather than site-specific solutions). Quantitative resilience methods are rare, and we are not aware of any for military applications (not related to mental health). Development of metrics for military settings will be a significant advance in the resilience community.

This approach will be more complex than existing VA methods. Information necessary for the development of conceptual models will be sensitive and require significant interaction. Adaptation of risk metrics to resilience metrics and evaluation of systems with cross-sector dependencies are known challenges in resilience analysis. The benefit will be a more comprehensive evaluation methodology, improving energy security.

Summary of Accomplishments:
Key scientific accomplishments include the following:
- Designed an electric power restoration model: this model enables one to determine impacts on load delivery to military facilities following disruptive events.
- Designed a mission dependency: this model enables one to evaluate impacts of power disruptions on the ability to meet mission objectives.
- Started software implementation of models: software codes are being written to numerically implement the mission and power restoration models.
- Started to develop a case study on how power disruptions affect completion of Sandia's missions: this case study will be used to validate and demonstrate the project's modeling and analysis tools.

Each of these accomplishments were key steps towards achieving the eventual goal of creating a toolset that can be used for modeling, analyzing, and quantifying how power disruptions affect the completion of military missions.

We also made significant progress towards developing key partnerships necessary to perform validation tasks. In July, the project was given a FY 2012 Technology Innovation Opportunity Award by Bonneville Power Administration. The award program is a competitive one in which researchers seek access to and collaboration with Bonneville staff. Our project was one of only 13 awardees, and this award will ensure that Bonneville staff collaborates during model validation efforts. We also have a verbal commitment from Kirtland Air Force Base to partner to develop additional test cases for validation.

The project made a number of presentations and publications. We have made three invited conference presentations, written an invited essay, and published a refereed journal article. We have briefed the project in a number of other forums, including meeting with TRANSCOM, DoD, Office of the Secretary of Defense (OSD), Chenega Support Services, and a number of internal Sandia seminars. Additionally, project members have been invited by CRC Press to write a book that details the resilience assessment approach leveraged by the project.

Significance:

Successful completion of this project will provide guidance for how the military should make investments across the military complex to increase energy security and decrease risk from possible disruptions to energy infrastructure systems, with the end result being increased national security. These methods will be of use to the US Army Energy Security mission, Defense Critical Infrastructure Program, Air Force Installations and Energy, and other similar missions. Additionally, the foundational methods developed under this project will be generally applicable to other homeland security areas such as DHS Infrastructure Protection and Continuity of Operations planning for a variety of federal agencies.

Refereed Communications:

E.D. Vugrin and R.C. Camphouse, "Infrastructure Resilience Assessment through Control Design," *International Journal of Critical Infrastructures*, vol.7, pp. 243-260, 2011.

Optimizing Infrastructure Investments in a Competitive Environment
151411

Year 2 of 3
Principal Investigator: R. L. Chen

Project Purpose:
In many complex systems, individuals or institutions compete for the use of a finite amount of infrastructure capacity. As examples, generation firms compete for transmission capacity and commuters interact in a de facto competition for highway capacity. In such complex systems, the optimization of infrastructure investments must take into consideration the impact of investment decisions on individuals or institutions competing for the use of these resources. However, many existing models assume a centralized resource planning approach where investment decisions are made in a coordinated fashion to maximize some measure of social welfare (e.g., minimizing overall system cost). Such coordinated system models are unrealistic in many cases where competition plays a crucial role. In a deregulated electric power industry, for example, generation investment decisions are made by individual institutions with little centralized coordination. In such cases, institutions make their decisions on the basis of expected future prices and returns on investments. Consequently, it is critical that decision makers consider the complex interactions amongst competitors when making infrastructure investments. This research will develop new models and optimization methods to effectively analyze Stackelberg games (leader-follower games) for infrastructure planning, specifically taking into consideration competition among the infrastructure users (followers). These models and optimization methods will allow decision makers to predict the responses of competing individuals and institutions to infrastructure investment decisions, analyze infrastructure investment risk, and perform sensitivity analyses to objectively trade off multiple system criteria.

Summary of Accomplishments:
In FY 2011, we focused on competition that is adversarial (as opposed to market driven). We developed bi-level and tri-level optimization models for infrastructure vulnerability analysis and augmentation. Bi-level and tri-level programs model the decision-making of both the infrastructure owner and that of an adversary, who is trying to inhibit infrastructure operations. We developed cutting plane algorithms for solving general tri-level optimization problems. We demonstrated, via computational experiments, using Institute of Electrical and Electronics Engineers test systems, that the new cutting plane algorithms using bi-level separation problems are more than two orders of magnitude faster than the standard decomposition algorithm. Results of this work appeared in one conference paper, one book chapter, and seven conference/workshop presentations.

Significance:
This project will develop optimization and analysis capabilities that are relevant to the energy security mission of DOE and to power grid design in particular. In addition, many Sandia, DOE, DoD and Department of Transportation missions will benefit from enhanced capabilities in the analysis of competition and adversaries in hierarchical systems, and advancements in computational models of these hierarchical systems.

Formation of Algae Growth and Lipid Production Constitutive Relations for Improved Algae Modeling
153236

Year 1 of 2
Principal Investigator: P. E. Gharagozloo

Project Purpose:
Algae-based biofuels have generated much excitement due to their potentially large oil yield from relatively small land use and without interfering with the food or water supply. Algae mitigate atmospheric CO_2 through metabolism. Production of algal biofuels will reduce dependence on foreign oil by providing a domestic renewable energy source. Important factors controlling algal productivity include temperature, nutrient concentrations, and the light-to-biomass conversion rate. Lipids produced by algae are easily converted into various fuels, but they must be generated in large quantities for efficient fuel production. The generation and regulation of lipids in the form of triacylglycerols (TAGs) is not well understood and needs to be studied to determine production levels under various conditions. Parametric studies of lipid-producing marine species, typically serial experiments, that use off-line monitoring of growth and lipid levels, are time consuming and incomplete. These are the necessary precursors for computational models, which currently lack the data necessary to accurately simulate and predict algae growth and lipid production. This project will begin with an algae growth and lipid production parametric study. Using innovative techniques to control temperature, nutrients, and light within a parallel growth apparatus, we will greatly decrease the time and mass of algae required to obtain fully parameterized growth and lipid formation constitutive relations. The knowledge gained will enable computational models to optimize algae growth in real-world conditions with varying temperature, light, and nutrient levels over the course of a day and year.

Summary of Accomplishments:
The overall goal of this project is to develop constitutive relations for our computational of growth and lipid production through parallelized multi-factorial experimental techniques. Our technical accomplishments in FY 2011 include the following:

Experimental:
- Developed experiments for measuring growth and lipid production of algae
- Completed growth and lipid measurements of *Dunaliella salina* varying light, salinity, and temperature
- Started grow up of *Nannocloropsis oculata*

Computational:
- Added salinity growth dependencies to Sandia's-EFDC/WQ (Environmental Fluid Dynamics Code/Water Quality) computational model
- Modified SNL-EFDC input files to model airlift type photobioreactors
- Developed tube-flow type photobioreactor model
- Developed constitutive relationships growth limitations for non-ideal salinity, light, and temperature conditions for *Dunaliella salina*
- Modeled *Dunaliella salina* in test tube airlift photobioreactor model to compare to measured data

Significance:
Algal biofuels have the potential to generate large oil yields with small land use, which will reduce our dependence on foreign oil and help ensure national energy surety. Algae growth in saline or wastewater is consistent with the tenets of Sandia's Energy-Water Nexus. This work will complement Sandia's current biofuel research portfolio and facilitate comprehensive modeling of real-world performance with more accurate constitutive relations.

The knowledge gained will enable computational models to optimize algae growth in real-world conditions with varying temperature, light and salinity over the course of a day, year or growth cycle.

Through a validated constitutive growth model, algae performance and production efficiency can be predicted for various growth conditions, including different weather climates and reactor designs. The model will enable improved design and algae strain selections.

Analysis of Gas-Lubricated Foil Thrust Bearings in Supercritical CO_2 Flow
153887

Year 1 of 2
Principal Investigator: T. M. Conboy

Project Purpose:
The DOE is currently in development of next-generation nuclear power reactors. In this aim, reactors using a closed-Brayton power conversion cycle have been proposed that have the potential to achieve higher outlet temperatures, higher thermal efficiencies, and reduced capital cost in comparison to current steam plants. The supercritical-CO_2 (S-CO_2) power cycle has been identified as a leading candidate for this application as it can achieve high efficiency at relatively low operating temperatures, with extremely compact turbo machinery. These attributes have also lead to interest in this power cycle for use with DoD and National Aeronautics and Space Administration's (NASA) power systems.

Sandia has been a leader in development of the S-CO_2 cycle, and is in possession of unique facilities for testing of turbo machinery in high-pressure supercritical fluid flow environments. One critical area not fully yet addressed for this technology is an analysis of the hydrodynamic and thermal behavior of the thrust bearings during turbomachinery operation. At present in the Sandia facilities, thrust-bearing performance has proven to be the factor limiting maximum compressor rotation frequency, but is not yet well understood. A model validated by experimental data is necessary for improved understanding of cycle performance and for greater accuracy in future feasibility assessments of the S-CO_2 cycle. The purpose of this project is to build a thrust bearings test rig to generate data at conditions representative of an operating S-CO_2 cycle, and to use this data to help develop a new hydrodynamic thrust bearings modeling code.

Summary of Accomplishments:
A review was conducted on different aspects of compliant foil thrust bearings and past modeling techniques. This identified gaps in previous modeling approaches, namely that many assumptions used previously break down in the two-phase, non-ideal, turbulent lubrication layer present in the case of high-pressure CO_2. Also, there was a startling lack of experimental test data in the literature.

First, analytical methods were used to integrate the Reynolds equation to obtain the "high-speed limit" for the Sandia bearings geometry in the limit of infinite runner speed. Next, a modeling code was created that divides the bearing thrust pad into radial and azimuthal nodes, over which the Reynolds equation was solved using second order finite difference methods. Solving the pressure field in the lubrication layer allowed calculations of load capacity, torque, and frictional power loss for the Sandia bearings design for a given speed and lubricant conditions. This model included deformation of the foil surface due to buildup of hydrodynamic pressure. Still, only laminar, isothermal films were considered. Future updates will incorporate turbulence and temperature dependency. A paper describing this model was published at the Supercritical CO_2 Power Cycle Symposium (May 2011).

Also the turbo-alternator-compressor unit from the Sandia S-CO_2 research loop was shipped to contractor Barber-Nichols where it was modified into a thrust bearings test rig. Other modifications were made at Sandia to allow for simulated thrust loads to be applied (using pressure differentials) and to allow high-speed torque measurements. Initial tests have been conducted and data analysis is under way.

Significance:
The completion of this study will lead to greatly improved understanding of thrust bearing performance under S-CO_2 flow. This work is necessary to further development of the Sandia S-CO_2 power cycle test loop. DOE has supported development of this facility, and it is one of the first and only S-CO_2 power production test loops in the world.

From the DOE perspective, the potential for improved thermal efficiency and capital cost of next-generation nuclear power plants puts this project directly in line with their core mission. The ability of the S-CO_2 power cycle to generate high efficiency with low to moderate temperatures implies that standard industrial materials could be used in construction of hot side piping and heat exchangers, further reducing costs.

Also, this cycle has garnered considerable interest for coupling with solar thermal, geothermal, and fossil fuel systems for improved efficiency. Recently, industrial partners have approached Sandia with proposals to utilize the S-CO_2 power cycle in gas turbine bottoming cycles and to help offset costs of carbon capture/sequestration (CCS) and enhanced oil recovery (EOR), power conversion in micro-turbines mounted the tops of solar towers and larger central solar thermal plants, power conversions using S-CO_2 based mixtures for high-efficiency generation in low temperature geothermal cycles, to name a few.

In addition to these interests, the large reduction in plant size, capital cost, and limited maintenance needs ally supercritical power cycles with reactors for military and space applications. All of these potential uses highlight the importance of continued development of the S-CO_2 Brayton cycle hardware to reduce risk for future commercial-scale systems.

Compact Reactor for Biofuel Synthesis
153889

Year 1 of 2
Principal Investigator: J. W. Pratt

Project Purpose:
Liquid fuels synthesized from renewable CO and H_2 could displace petroleum-based fuels to provide clean, renewable energy for the future. Small-scale (<100 bbl/day) reactors for synthetic liquid fuels production (e.g., methanol, Fischer-Tropsch diesel) are an emerging development area that may enable the use of diverse, renewable, carbon-neutral feedstocks, such as biomass. For small-scale production of synthetic liquid fuels from syngas, fixed-bed reactors are most well suited and have the highest potential productivity per reactor volume. To fully realize the potential of these reactors, four key issues must be addressed: 1) minimize temperature gradients due to the highly exothermic reactions, 2) maximize diffusion of reactants and products, 3) prevent heavy hydrocarbons (waxes) from accumulating in the catalyst pellets, reducing conversion, and 4) management of lifecycle degradation. Addressing these issues requires validated, coupled, heat and mass transport and chemical kinetics models. Although a large body of work exists in modeling Fischer-Tropsch reactors, current liquid fuel synthesis models are largely empirical. While useful for predicting performance of traditional large-scale, coal-to-liquids reactors, these existing models lack sufficient fidelity to enable examination of small-scale reactors or unique designs.

The purpose of this work is to create a gas-to-liquids (GTL) synthesis model with the minimum amount of empiricism and assumptions allowed by the current state of the theory. The modeling method required to accomplish this is a component-based, dynamic (time-varying) two-dimensional heterogeneous model that accounts for interfacial and intraparticle gradients. The difficult nature of both the theoretical development and mechanics of the computational simulation has led to no evidence in the open literature of a model of this type ever being successfully developed. The successful, validated model will enable accurate simulation of innovative and non-traditional GTL reactors for the first time.

Summary of Accomplishments:
Programmed and verified (in COMSOL multiphysics software) initial component models for three of the six components in the full model: interparticle mass transfer, interparticle heat transfer, and Fischer-Tropsch chemical kinetics. Coupled mass transfer with kinetics.

Significance:
Biomass-derived liquid fuel production is recognized as an important component in secure domestic energy supplies as well as in the remote supply of military logistic fuels. In addition, this research has a direct relationship to the processing and conversion research area of the DOE's Office of the Biomass Program (OBP). In this area, the thermochemical conversion platform's current DOE-sponsored research has a clear gap in the fuel synthesis area that this work addresses through fundamental reactor understanding (and eventual design). Although industrial partnerships will be utilized for guidance and validation, the results of this work will be open.

The work to date provides the foundation of a general, integrated model for predicting gas-to-liquids synthesis.

Development of a Raman Spectroscopy Technique to Detect Alternate Transportation Fuel Hydrocarbon Intermediates in Complex Combustion Environments
154319

Year 1 of 2
Principal Investigator: I. Ekoto

Project Purpose:
Existing validation datasets for predictive combustion simulations are incomplete partly due to the inadequate capabilities of currently applied experimental methods. A major gap remains the inability to directly and quantitatively measure hydrocarbon fuels more complex than methane and combustion intermediate concentrations, which are necessary to characterize reaction progress variables. This gap can be bridged by taking advantage of recent advances in Raman-based detection techniques and through the diagnostic developments in this project. The challenge is to differentiate overlapping, temperature-dependent Raman spectral signatures from hydrocarbon fuels and their combustion intermediates and convert that information into accurate concentration measurements. Since laminar flame calculations indicate hydrocarbon speciation strongly depends on fuel type and combustion environment, the developed method must be broadly applicable.

Preliminary Raman spectroscopy measurements from laboratory flames of dimethyl ether (DME), a promising alternative transportation fuel, suggest that it should be possible to deconvolve individual spectral contributions from the parent fuel and its main, stable hydrocarbon combustion intermediates and convert this information into quantitative concentrations. Application of this technique, however, requires detailed spectral information about each stable hydrocarbon species and newly developed analysis tools for signal postprocessing and data interpretation.

For the proposed study, Raman spectral libraries for important hydrocarbon fuels and combustion intermediates will be recorded over a broad range of temperatures using the multiscalar measurement facility located at Sandia California. Recorded spectra will be converted into synthetic spectral libraries and incorporated into novel spectral analysis models that account for spectral crosstalk from the unknown hydrocarbon concentrations and iteratively find the unknown flame temperature. Performance testing of developed libraries and reduction methods will be conducted through an analysis of results from heated mixtures at known compositions and from well-characterized laminar reference flames. The diagnostic represents a first-of-its-kind measurement technique that can be used to temporally and spatially resolve speciated hydrocarbon concentrations during combustion.

Summary of Accomplishments:
We fabricated necessary hardware including a custom quartz tube burner that was used to supply heated gas samples to the test section for the desired Raman spectral measurements. Nitrogen diluted test gases are fed through inlet ports in the burner base at low supply rates (<25 liters/min) to ensure laminar exit flows. Test gases are heated to desired temperatures, up to 900 K, via an elongated silicon carbide heater located in the tube base and controlled by a variable autotransformer. Raman spectra of important intermediate hydrocarbons (methane, acetylene, ethylene, ethane, and dimethyl ether), identified from laminar flamelet calculations of dimethyl ether flames, were acquired using the quartz burner at room temperatures on up to the 900 K limit in 100 K increments. Spectra at more representative flame temperatures were acquired from conditionally averaged laminar flat flames. An additional hydrocarbon of interest is formaldehyde; however, this molecule is inherently unstable in the gas phase and cannot be stored by the laboratory gas handling system. To resolve this problem, vaporized methanediol (or

formalin), which is a saturated aqueous solution that contains 37% formaldehyde, will instead be used. Above 700 K, methanediol rapidly decomposes back to formaldehyde and water that can then be passed through the gas heater. A suitable boiler has been identified, and is currently being integrated into the multiscalar measurement facility.

A skeletal data post-processing program has been developed and validated against earlier spectral measurements from simple methane flames with little contribution from hydrocarbon intermediates. The program is a MatLab-based graphical user interface (GUI) that allows users to input the gas and oxidizer compositions, specify molecules to exclude from the reduction algorithm, and accounts for various spectral crosstalks from major species. Final versions will enable interpretation of measured Raman spectra from flames with substantial intermediate hydrocarbon contributions.

Significance:
Predictive simulation based design of combustion devices holds the promise to produce cleaner and more efficient engines. Efficiency gains of 20-50% can substantially enhance national energy security while helping mitigate the effects of climate change. However, current predictive simulations offer limited accuracy due to lagging science-based development of simulation submodels, which is hindered by a lack of high-fidelity measurements from well-characterized combustion experiments. The proposed work will develop new diagnostic capabilities that overcome some of these shortcomings and accordingly will benefit the DOE Energy Security and Scientific Discovery and Innovation missions.

Polymer-MOF Nanocomposites for High Performance Dielectric Materials
155065

Year 1 of 3
Principal Investigator: L. Appelhans

Project Purpose:
Capacitors for power electronics, pulsed power, and energy storage applications require high energy densities, high dielectric breakdown strengths, and high temperature operating capability while maintaining the ability to fail as an open rather than as a short. Current dielectric technologies do not meet these requirements. Energy densities must increase by an order of magnitude in order to satisfy future needs. This goal is impossible to achieve without the development of new dielectric materials. Polymer nanocomposite dielectric materials have demonstrated superior properties relative to dielectrics based on ceramics or polymers alone. However, a major challenge in the development of nanocomposite materials is nanoparticle dispersion. Nanoparticle agglomeration severely diminishes the practical utility of dielectric polymer nanocomposite materials through degradation of dielectric properties and poor reproducibility and scalability. We propose to develop polymer nanocomposite dielectric materials with metal organic frameworks (MOFs) as a solution to this fundamental problem. Current methods to minimize agglomeration rely on surface functionalization of inorganic nanoparticles, but these techniques introduce complication and expense related to the surface functionalization step. MOFs have built-in organic moieties on the surfaces that will improve intrinsic particle compatibility without additional functionalization. Polymer-MOF nanocomposites provide a very attractive solution to challenges in dielectric development that, if not overcome, will impede the realization of a practical electrical infrastructure.

The field of polymer nanocomposites is one of the most promising areas to provide materials solutions to research challenges in a wide range of critical areas, including energy, transportation, and weapons safety and security, if fundamental barriers can be overcome. Current research in MOF polymer nanocomposites is extremely limited and not well understood at a fundamental level. The proposed research will position Sandia with an early expertise in an area at the intersection of two rapidly growing fields in which there is a high potential for groundbreaking research with relatively low investments in time and financial commitments.

Summary of Accomplishments:
The following milestones have been accomplished.

- MOF nanoparticles of type ZIF-8 (zeolitic imidazolate framework 8, zinc 2-methylimidazolate) have been synthesized in a range of sizes from 20nm to 600nm, as reported in the literature. Composites with a high temperature copolymer were made with varying loadings at each of the different particle sizes. The dielectric characteristics (permittivity, breakdown strength) were measured and comparisons between different ZIF-8 samples and inorganic (titania) composites were made.
- The MOF composites were found to have improved breakdown strengths relative to the inorganic composite, although breakdown strengths of both types of composites were lower than polymer alone. All composites had higher permittivities than the polymer alone. The breakdown strengths and permittivities of the MOF composites were found to be highly dependent on particle size and dispersion, with the best performance observed for composites of ~60 nm particles.
- Higher weight percent loadings (30 wt%) of particles generally had lower breakdown strengths than lower loadings (10 wt%). Microscale particles of a barium tartrate MOF, BaTar, were synthesized and 10 wt% polymer composites were made. Electrical measurements showed that the permittivity of the composite was greater than the polymer alone, while the breakdown strength did not differ

significantly between the composite and the polymer alone. This is a very encouraging result as breakdown strengths of composites are often lower than that of the pure polymer.
- Attempts to synthesize nanoparticles of the BaTar MOF via direct synthesis were unsuccessful but nanoparticles in the 200-300 nm range were synthesized by ball milling. However, comparisons between ball milled and as-synthesized BaTar samples incorporated into films show no significant performance differences. The dielectric properties of pure MOF materials pressed into pellets are being investigated for relationships to structure and composition as well as possible sensing applications based on changes in dielectric properties.
- In the ZIF-8 MOF polymer composite system studied, the greatest increase in dielectric permittivity, relative to the control polymer, was observed for composites using ~60-nm monodisperse ZIF 8 particles, which dispersed well under the synthetic conditions. Smaller particles (~20 nm), which tended to form more agglomerates, resulted in a smaller relative increase in dielectric permittivity. Large (~600 nm) particles that dispersed well also resulted in only moderate increases in permittivity. Composite systems thus must be optimized for the smallest particle size that continues to allow for thorough dispersability. The particle size and dispersion also affect breakdown voltages, but the dependence is more complicated. In another system (metal tartrate MOFs-polymer composites), post-synthetic ball milling controlled particle size and different effects on dielectric characteristics were observed. Reduction in average particle size from >2-3 microns to <1 micron led to improved breakdown voltages in composites made from the smaller particles, but there was not a significant difference in the permittivity between composites of the two sizes. This suggests that there may be a size threshold in the hundreds of nanometers range, above which particle size does not have as significant of an effect on permittivity. This would agree with other work showing the volume of polymer-filler interface is a key factor affecting permittivity.

Significance:
This project has improved the level of understanding of MOF-polymer composites and the effects of structure, composition, particle size, and dispersion on their dielectric properties. It has shown that particle size and dispersion greatly affect the permittivity of MOF-polymer composites. An interesting correlation between structure polarity (chirality) and dielectric permittivity has been observed in the barium tartrate compounds. Although both these effects are intuitively reasonable, this direct relationship between structural chirality and permittivity has not been demonstrated before in MOFs. This understanding of the underlying relationships between structure and dielectric properties in MOFs, in addition to its value as fundamental knowledge, will also significantly improve the ability to prescreen MOF materials, based on structure and composition, to identify promising candidates for composite or pure dielectric applications.

The study of MOF-polymer composites addresses needs for novel dielectric materials for use in high performance capacitors (DOE Office of Energy Efficiency and Renewable Energy [EERE)] Defense Advanced Research Projects Agency, Office of Naval Research). Development of a fundamental understanding of MOF-polymer nanocomposites could translate to advances in other areas such as gas or chemical sensors (DoD, DHS, and Defense Threat Reduction Agency), polymer electrolytes for next generation batteries and fuel cells (DOE's Basic Energy Sciences, EERE), membranes for gas separation or water treatment, and composite materials (DOE).

Time-Resolved Broadband Cavity-Enhanced Absorption Spectrometry for Chemical Kinetics
155298

Year 1 of 3
Principal Investigator: L. Sheps

Project Purpose:
Experimental measurements of elementary rate coefficients and branching ratios are essential to our understanding of important reaction mechanisms in combustion chemistry. However, such measurements are often impossible because of a lack of adequate detection techniques. Short lifetimes and low concentrations of many reactive intermediates, together with competing reactions and wall effects, impose the following demands on the ideal experimental detection method: 1) nonintrusive probing of homogeneous reaction zones, 2) simultaneous detection of multiple species, especially important for complex reactions, 3) time resolution $<10^{-5}$ s for real-time monitoring of species concentrations, and 4) high sensitivity ($<10^{10}$ molecules·cm^{-3}).

Current detection techniques, including conventional absorption or Raman spectroscopy, laser-induced fluorescence, and photoionization mass spectrometry, do not meet all four requirements simultaneously. To address this challenge, we are pursuing a general detection method that does fulfill all of these requirements and will enable efficient experimental measurements to validate predictive simulations of gas-phase chemical kinetics.

Our innovation is to implement the proven high sensitivity of cavity-enhanced optical absorption in a unique multiplexed frequency- and time-resolved spectrometer. We will use a photolysis laser pulse to initiate chemical reactions in a flowing gas mixture and monitor the ensuing kinetics by broadband transient absorption inside an optical buildup cavity. The multipass cavity will provide very long effective absorption path lengths, ~200 m, across a broad spectral range, 300 –800 nm. For many key combustion intermediates (e.g., vinyl, allyl, formyl, and propargyl radicals) such long absorption paths will give detection levels $<10^{10}$ molecules·cm^{-3}. The probe cavity output will be simultaneously dispersed in frequency (by a ruled grating) and in time (by a rapidly swept mirror) along orthogonal spatial directions and projected onto a charge coupled device (CCD) camera. Time evolution of a broad transient absorption spectrum will be recorded in a single shot with μs-level time resolution.

Summary of Accomplishments:
This year, we have completed the design of the experimental apparatus and began its construction and optimization. We installed two separate light sources (a simple Xe arc lamp and a more sophisticated supercontinuum laser). In addition, we worked with an outside specialty optics company to design and manufacture a set of broadband high reflective mirrors — one of the main technical challenges of this project. The mirrors have a reflectance of 99.5 ± 0.2% at wavelengths from 370 to 700 nm — an unprecedented level of performance over such a broad range. We have measured the finesse of the cavity using both light sources and found that its performance matches expectations very closely — within a factor of 2. Further work on improvement in the buildup quality is ongoing.

We have purchased and installed the optical detector — a high-performance low-noise CCD camera. We have also designed the data acquisition system and written the necessary software to interface with the camera. Finally, we have constructed a robust homebuilt spectrometer using simple ruled gratings and verified its performance.

The spectrometer is ready for final optimization and calibration with known absorption standards. We plan to perform the calibration early in FY 2012. Concurrently, we plan to construct the sample delivery system — gas lines, pressure and flow control, and pumping. After that, we plan to add the time-resolved signal detection capability that will complete the spectrometer construction phase.

Significance:
The proposed research will provide a new state-of-the-art experimental technique for direct measurements of gas-phase reaction kinetics. The new method will significantly expand existing capabilities for evaluating and optimizing the performance of novel fuels in the search for clean, efficient energy supplies as alternatives to petroleum-based sources. Therefore, this proposal aligns closely with the DOE Energy Security Mission.

Accelerating the Development of Transparent Graphene Electrodes through Basic Science-Driven Chemical Functionalization
155550

Year 1 of 3
Principal Investigator: C. Chan

Project Purpose:
Despite intense research on the fundamental properties of graphene since its isolation in 2004, its practical widespread application remains elusive. Graphene has been proposed for use as a transparent electrode owing to the material's high in-plane conductivity, transparency, chemical stability, and elemental abundance. Large interest in this application stems from the desire to replace rare and expensive brittle conducting oxides (e.g., indium tin oxide [ITO]), unstable conducting polymers (e.g., Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)PEDOT:PSS), and fragile optically thin metals as electrical contacts to solar cells, light-emitting diodes, and photodetectors. However, previous efforts in using graphene for electrodes have suffered from poor film quality and uncontrolled interactions between graphene and the contacted materials. Chemical functionalization is a promising means of modifying and improving graphene's interaction with other materials, but current functionalization schemes are not well controlled, characterized, or understood. The practical use of graphene as a transparent electrode material will require controlling the chemical functionalization of graphene interfaces, characterizing the physical properties of the functionalized surfaces, and understanding how modifying graphene's chemical nature also affects its material and physical properties.

This work employs a comprehensive characterization methodology to understand the effects of functionalization chemistry on the material and physical properties of graphene. Of particular interest is how chemical functionalization of graphene affects its electronic band structure and its energy band alignment with other materials. These issues, which are still not well characterized or understood in graphene, greatly affect the material's conductivity and transparency, as well as charge injection and extraction in devices. We are initially investigating functionalization chemistries intended to modify the work function of graphene and improve its performance as a transparent electrode in optoelectronic devices. Using knowledge generated from fundamental surface science measurements, and correlating functionalization chemistries to material properties, this project's work will accelerate the systematic development of optimally functionalized graphene films for transparent electrodes and other applications.

Summary of Accomplishments:
We demonstrated controlled basal plane chemical functionalization of near-perfect epitaxial graphene grown on n-6H-SiC(0001). Functionalization was achieved by electrochemical reaction of graphene with bis(4-trifluomethylphenyl)iodonium tetrafluoroborate immersed in a tetrabutylammonium tetrafluoroborate buffered acetonitrile solution. Cyclic voltammograms of the reaction indicated a reduction wave at -1.0 V versus Ag/Ag^+, which is correlated to the reduction of bis(4-trifluomethylphenyl)iodonium molecules into free CF_3-aryl radicals, and their ensuing chemisorption onto graphene. Saturated coverage of graphene was achieved using cyclic voltammetry, or chronoamperometry in the diffusion-limited regime. Controlled sub-monolayer coverages were obtained using kinetically limited chronoamperometry in which voltages were limited to near the onset of the reduction wave. Detailed characterizations of the CF_3-aryl-graphene films were conducted using scanning Raman spectroscopy (SRS), ultraviolet photoemission spectroscopy (UPS), and x-ray photoemission spectroscopy (XPS). We learned from SRS that functionalization was uniform over graphene, and increased "defect" peaks likely resulted from breaking of graphene's two-dimensional

symmetry. Interestingly, the functionalization chemistry created regions with differing strain that likely conform to the initial growth characteristics of the graphene film on SiC. We learned from UPS studies that physisorbed CF_3-arylene decreases graphene's work function by 0.2 eV due to a "pillowing" effect, and that chemisorbed CF_3-arylene increases graphene's work function by 0.7 eV due to electron transfer from graphene to fluorine moieties. Electron transfer between graphene and the outermost moieties of CF_3-arylene indicate formation of chemical bonds as also reflected in UPS by a shift of graphene's electronic pi states to localized higher binding energy states. The latter is consistent with saturation of sp^2 and pz orbitals of graphene by chemical bonding with CF_3-arylenes. XPS results confirm these UPS findings. We have also completed the commissioning of laboratory infrastructure required for the success of this project, as well as preliminary studies of NO_2-aryl functionalization of ITO.

Significance:
Many technologies driving US innovation, commercial interests, and national security rely heavily on transparent electrodes based on scarce and expensive minerals controlled by foreign entities. Many energy conversion technologies requiring efficient electrical contacts are also needed for a balanced, independent, and sustainable national energy portfolio. Successful implementation of this project could have an impact on mitigating our nation's reliance on foreign resources, and bolster the diversity and sustainability of our own energy resources. This work will also have consequences in wide-ranging engineering applications, such as nanoscale processing of graphene for national security applications in nanoelectronics and chemical/biological sensing. Arylene functionalization serves not only as a proof of concept for more directed functionalization schemes, but it can also be leveraged as linkage groups for attaching more specific functionalization groups to graphene. The observed changes in graphene's electronic structure are promising for tailored properties in realizing practical graphene applications such as patterning, integrated circuits, quantum wells, and transparent electrodes. Our key R&D accomplishments have been recognized by other Sandia and external researchers. This work has already resulted in collaboration with University of Texas-Austin (UT-A) researchers. In particular, the UT-A/Sandia Energy Frontiers Research Center in Charge Separation and Transfer will leverage the use of graphene as an ideal template for functionalizing and preparing well-ordered molecular substrates for studying fundamental charge separation and transfer phenomena in photovoltaic and energy storage devices. Potential collaboration with other internal projects in tunable graphene infrared detectors and graphene permeation barriers is being explored.

Aerosol Characterization Study Using Multi-Spectrum Remote Sensing Measurement Techniques
155804

Year 1 of 3
Principal Investigator: C. C. Reed

Project Purpose:
Atmospheric aerosols affect climate both directly through scattering and absorption of solar radiation and indirectly by serving as cloud condensation nuclei or ice nuclei. Because of the complex spatial and temporal variability of atmospheric aerosols, measurements of the vertical structure of physical, chemical, and optical properties are necessary to understand the effects of aerosol concentrations on global climate. Light detection and ranging (LIDAR) remote sensing techniques have been employed to measure the vertical structure of atmospheric aerosol concentrations. However, due to a lack of laboratory comparisons linking LIDAR backscatter to the physical and chemical properties of in situ aerosols, empirical calculations are often used as an intermediary to estimate such properties. Furthermore, the majority of current LIDAR systems only use a few select wavelengths. This limits the characterization of the chemical distribution of aerosols present and directly impacts single scattering albedo calculations, a parameter used by climate modelers. It is my hypothesis that the wavelength specific scattering properties of atmospheric aerosols are strongly dependent on composition. Through the synergy of a multi-spectral LIDAR and experimental methods, both the particle size distribution and more detailed characteristics of the ambient aerosol particle can be found. By bringing together a multidisciplinary team of researchers, utilizing advanced experimental facilities, and working with powerful computational resources, this project is at the cutting edge of research and development. Detailed LIDAR-retrieval algorithms across a broad range of wavelengths are being developed using an advanced aerosol chamber coupled with a small multispectral LIDAR system. Through the course of experimental research, there is an associated risk due to the unknown wavelength dependence of the particle backscatter on chemical composition. Therefore, it will be necessary to identify the wavelengths responsible for detailing particle composition. Following completion of laboratory experiments, data will be integrated into an algorithm to measure atmospheric aerosols using an existing Sandia system.

Summary of Accomplishments:
To date, significant advancement has been made toward the overall technical goals and milestones of this project. Key organic chemicals of interest have been identified, and the coinciding particulate generating gaseous concentrations necessary have been established to generate a high concentration of atmospheric organic particulates within a sealed Teflon cloud chamber. This Teflon cloud chamber has been designed and ordered from American Durafilm Corporation, Inc. It was determined that laboratory generation of organic and secondary organic aerosol will require a low concentration of ozone mixed with a preset concentration of organic gases (toluene, isoprene, m-xylene, and p-xylene, to name a few). The oxidation process, over time, will lead to low volatility compounds that condense into the particle phase. The particulate concentrations within the Teflon chamber will be monitored to ensure that a high concentration exists to provide sound optical measurements within the flow tube. Furthermore, the flow chamber has been fully characterized using Arizona Road Dust (fine grade). This was done by performing flow measurements, utilizing fluid dynamics models to map the flow pattern within the chamber, measuring the pressure of the system during operation, and measuring the particle size distribution at various radial and axial positions within the measurement tube. Arizona Road Dust was generated using two separate aerosol dispersion devices, the Palas rotating brush generator (RBG) and

the fluidized bed aerosol generator. Both methods of powder dispersion were found to produce relatively stable aerosol concentrations in the chamber with the RBG exhibiting less variability. Inorganic powder aerosol dispersion will, therefore, be aerosolized using the RBG for future optical measurements. This was a necessary step toward integrating the laser system and is listed as a key future milestone of the work.

Significance:

The work will support DOE's mission in climate and atmospheric monitoring as well as to strengthen scientific discovery and innovation. By providing the data necessary to measure the atmospheric aerosol composition on large scales both regionally and globally, this work will enable the determination of the effects of aerosol concentrations on climate and human health. Data obtained from optical measurements will also be necessary in understanding our nation's ability to detect and identify biological aerosol plumes in a background urban aerosol. Furthermore, this work will provide the basis for understanding the age and origination of anthropogenic plumes, a necessary component in determining the impacts of foreign plumes on our nation's pollution levels and treaty verification.

Use of Limited Data to Construct Bayesian Networks for Probabilistic Risk Assessment
156135

Year 1 of 3
Principal Investigator: K. Groth

Project Purpose:
Probabilistic Risk Assessment (PRA) is a fundamental part of safety/quality assurance for nuclear power and nuclear weapons. As energy and defense systems change, PRA must evolve to accommodate technological advances (e.g., digital instrumentation and control automation; passive components), and existing soft, causal risk areas (e.g., aging, common cause failure, human reliability analysis [HRA]).

Traditional PRA very effectively models complex hardware system risks using binary probabilistic models. However, traditional PRA models are not flexible enough to accommodate nonbinary soft-causal factors. Bayesian Networks (BNs) offer graphical and mathematical framework to address these challenges.

BNs are difficult to construct for most applications, but PRA applications face additional challenges because of event rarity, limited data, and system interdependencies. While there has been increased interest in BNs in PRA, there is little guidance on how to synthesize limited information to build them. This project aims to produce a data-informed BN for HRA, and to establish expertise and analysis capability at Sandia for construction and use of BNs to improve PRA. BNs are frequently used in applications where there is either ample data or no data. For HRA, there is probabilistic information available, but it is in various forms (quantitative, qualitative) and small quantities, which makes network quantification challenging. Bayesian quantitative methods have a long history of use in PRA, but only recently have they been proposed for HRA. Bayesian Networks go further than Bayesian quantitative methods by introducing a graphical structure; this enables HRA to be fully integrated with PRA models.

The research is at the intersection of several challenging PRA research areas. It improves both the representation and the quantification of complex, nondeterministic system elements in the face of substantial uncertainty. This research improves the way that PRA analyzes human risks and builds a foundation to integrate increasingly complex socio-technical systems into decision-making.

Summary of Accomplishments:
The primary goal for FY 2011 was to explore methods for building Bayesian Networks (BNs). This entailed a literature review and exploration of software tools. The literature review will be completed by the end of FY 2011. We became familiar with two software tools: Hugin (Nykredit, Inc.) and GeNIe. The Hugin software package was selected for the next research phase. We explored two structural learning techniques (constraint-based condition and necessary path condition) for developing models from data. Using two sources of data, we built prototype graphical structures using the learning techniques in Hugin; structural learning is a promising direction, but the algorithms were unable to learn a structure for some variables in the data. This work proved that it is possible to machine-learn structures of Bayesian Networks using human performance data from a single source; this is the first attempt to apply these techniques within the HRA field. However, it also demonstrated that no single source of current data is sufficient to produce a full network. During FY 20l1, we also identified several new sources of human performance data for high-reliability industries. The principal investigator attended a

Nuclear Regulatory Commission workshop on data collection for HRA. We identified nine sources of data relevant to human performance in nuclear power plants and we gained access to six of the data sources as of June. We are pursuing options to obtain the three additional data sources. We began documenting properties of the data sources that would make them suitable for combination in a single causal model. As of June, we have reviewed five of the nine data sources; one source is believed to be very promising, but the other four data sources have limited possibility to be used for quantitative purposes. At least two of the remaining data sources appear to be usable.

Significance:
Ensuring safe energy is central to the DOE mission, and PRA is a fundamental part of ensuring safety. This research will directly improve nuclear power plant safety via an improved HRA model. Recently, there has been a push to use data to reduce the subjectivity of the HRA models currently used in nuclear power plant PRA. The Nuclear Regulatory Commission has ongoing research in HRA data collection and this work has garnered international interest, but no research group has addressed how to use this data in quantitative modeling.

BNs provide the conceptual framework to combine different forms of information, but this has never been done in a PRA application. This work explores various sources of data relevant to human performance in nuclear power plants, and explores techniques for synthesizing the information into a BN. This is the first modeling effort of its kind and the resulting model will transform the way that human error probabilities are estimated for PRA. This project proactively addresses a challenge for energy safety, while also building important capacity at Sandia. This capacity is important to maintain Sandia's world-renowned reputation for advanced PRA, and to position Sandia to address the next generation of modeling challenges for high-consequence industries. The ability to build Bayesian Networks with scarce data provides a unique capability; this can be leveraged for PRA and decision-making in myriad applications, including nuclear power, nuclear weapons and defense.

Smart Adaptive Wind Turbines and Smart Adaptive Wind Farms
156702

Year 1 of 3
Principal Investigator: J. White

Project Purpose:
At the end of Q3 2010, the United States was the largest producer of wind energy with ~2% of all energy supply coming from wind. Although the percentage is single digit, wind energy is currently the most viable clean energy source and has represented ~40% of all new energy. To improve reliability and efficiency, smart adaptive turbines are needed that have the ability to actively measure and control the magnitude and distribution of forces applied to the rotors and drivetrain in order to maximize performance, minimize imbalance loads, diagnose and regulate the growth rate of damage, and optimize operations and maintenance costs. None of these advancements are possible without the development of an advanced operational monitoring system that will enable smart adaptive turbines. Sensor and data acquisition systems currently deployed on turbines do not have the capability for performing these tasks. Current domestic and international research programs have been focused on the development of component level technology, but have not yet recognized the highly coupled nature of turbine structural dynamics which dictates the need for a unified turbine operational monitoring system.

The research in this project addresses this need and is complex, crosscutting, and forward-looking in nature. Development of this technology will be challenging because some critical physical phenomenon in the complex motion of an operating turbine may not yet be modeled.

Summary of Accomplishments:
In this initial phase, the emphasis of the research has been to align resources and experiments that support the development work to be performed in FY12-13 in order to avoid delays that could impact the outcome. To develop next-generation operational monitoring systems for wind energy plants, computational simulations and real-world experiments are required. We worked to gain access to structural and aerodynamic sensor data from the Sensored Rotor 2 and SMART Rotor Systems, Inc. experiments; these were performed on a subscale 100-kilowatt (kW) wind turbine by Sandia's Wind Energy Department. The project work will be an expansion of the intended use of the multimillion-dollar data.

The subscale data from Sandia is invaluable; however, at the 100 kW scale the data may be missing some of the important physics encountered by a utility scale multi-megawatt (MW) wind turbine. Installation of turbines at this scale and experiments easily cost on the order of millions of dollars, therefore, to get access to such data the project has worked to develop a collaborative relationship and Memorandum of Understanding with the University of Minnesota 2.5 MW Clipper research wind turbine. In this collaboration, the project has enabled us to advise and support the selection and installation of instrumentation and data acquisition on the turbine. In exchange, we will receive the raw data for use in the project for utility-scale research and development.

To process all of this data at the highest technical levels using the least amount of labor time, the Test.Lab software from LMS (Learning Management System) Corporation has been purchased. The processed data will be used to produce highly validated wind turbine models and results that will then be used with advanced signal processing to achieve the goals of this project.

Significance:
Advanced sensing systems are required for the future of wind energy production. We envision these systems as determining the load and state of each wind turbine and we will combine them into an integrated wind farm control. Control at the wind farm level will allow for an unprecedented ability to optimize the long-term revenue, which is a balance between energy capture, operations and maintenance costs, and ancillary grid services. This will allow for a dramatic reduction in costly unscheduled maintenance and the possibility of derating damaged turbines slightly to dramatically increase the time until maintenance. Furthermore, the damage growth rates of many turbines could be changed to drive maintenance activities to occur at a synchronized time for reduced operations and maintenance costs through economies of scale. An example of economies of scale would be to distribute the cost of moving and assembling a maintenance crane over many synchronized turbine repairs, as opposed to the cost to repair turbines individually.

The outcomes of this project should enable new funded research and development activities in smart wind farm control, structural health monitoring (particularly offshore), sensing, and optimized revenue-driven wind turbine control. The new developments in operational estimation and damage monitoring will benefit existing and expected new research projects in wind energy, marine hydrokinetic energy, and solar.

Operational monitoring technology developed in this project is equally useful and beneficial for other rotating structures and/or large civil structures, such as rotorcraft and offshore drilling platforms. Identification of distributed forces, deflections, and state of structural health would be useful for improving the reliability and performance in these applications. Relevant agencies include the DoD, DOE, and DHS. The general S&T community has already benefited from this work through our efforts to develop technical tracks at the International Workshop on Structural Health Monitoring 2011 (IWSHM) and at the National Renewable Energy Laboratory Condition Monitoring Workshop (NREL). At IWSHM, nine papers were accepted for publication. At NREL, four papers were accepted for a session on structural health monitoring of wind turbines.

Refereed Communications:
J.R. White, "Passive Damage Monitoring of Wind Turbine Rotor Blades Using Cyclic Signal Processing," in proceedings of the *International Workshop on Structural Health Monitoring 2011,* CD-ROM.

Fluid Flow Measurement of High-Temperature Molten Nitrate Salts
157145

Year 1 of 3
Principal Investigator: A. M. Kruizenga

Project Purpose:
Current working fluids for concentrating solar power (CSP) applications must achieve very high temperatures, in excess of 650 °C, to meet operational and efficiency goals for power production, with nitrate salts as one suggested heat transfer fluid. Unfortunately, much of the industrially available instrumentation for flow and pressure measurement is not rated for use above 450-500 °C. The temperature limitations on most flow devices can be attributed broadly to materials compatibility. The ideal flow measurement device would be corrosion resistant, have minimal or no moving parts to minimize failures at high temperatures, and could be scaled from an R&D prototype to an industrial-sized device. For instrumentation development to be realized, the first challenge would be to engineer and build a flowing molten facility at Sandia California. The specific technical challenge would then be to develop and test several different flow and pressure measurement devices that operate up to 700 °C with a flow error of less than 5%.

Technology currently exists for flow detection of ionic liquids at moderate temperatures (420 °C). The innovative nature of this work would expand current technologies and develop a prototype that is capable of withstanding the extremely high temperatures (~700 °C) desired for continuous operation in molten nitrate salts, while producing reliable and repeatable measurements of important flow parameters. Building an R&D molten salt loop will allow for the development of new materials suitable for use in high temperature molten salt systems, such as packing material for valves, pressure measurement techniques, and gaskets.

Summary of Accomplishments:
We learned that this sensor concept is not as well understood as initially suspected. Having a redirection where an initial prototype can be tested at near ambient conditions allows better insight into the design parameters for this device. This project is in the beginning stages, with preliminary designs for several sensors to be evaluated. Fabrication of an experimental prototype is already in process with safety reviews already completed.

Significance:
This work fits under the DOE's Solar Technologies mission, under Energy Efficiently and Renewable Energy (EERE). More specifically this targets the CSP subprogram that seeks to make CSP competitive by reducing system and operational costs, which parallels the DOEs theme of energy security. This work has the potential for introducing a flow meter type that can measure fluids at high temperature, where such a device currently does not exist.

Hydrological Characterization of Karst Phenomenon in a Semiarid Region Using In-situ Geophysical Technologies
157311

Year 1 of 3
Principal Investigator: K. S. Barnhart

Project Purpose:
We propose to pioneer a new geophysical method for characterizing the hydrodynamics of semiarid karst. The dissolution of soluble bedrock (e.g., limestone) results in surface and subterranean channels, called karst, which comprises 7% to 10% of the dry earth's surface. Karst serves as a preferential conduit to focus surface and subsurface water but, because of irregular structure and nonlinear hydrodynamic behavior, is difficult to exploit as a water resource or protect from pollution.

Municipal/agricultural/energy/carbon storage/waste projects are projected for location in semiarid regions, where karst often exists but is essentially impossible to characterize using standard "wet karst" methods. Hence, the scientific challenge is to develop new techniques to gather karst hydrological information in terrains where karst features are dry except during infrequent rain and runoff events. Ground-based geophysical tools are typically chosen to locate karst structural features when water is limited or absent. Unfortunately, past field studies have met limited success because aforementioned subsurface heterogeneities confuse low-resolution data. Even when karstic conduits are located, the original questions, pertaining to conduit hydrological significance, are left unanswered. We are customizing emerging in situ geophysical monitoring technology to generate time-series data during sporadic rain events. Electrical and seismic sensors will be connected to wireless "nodes" that can be left in the field for many months. Embedded software will increase sampling frequency during periods of rainfall. Further, we will develop parallel inverse code to determine subsurface parameters from this unique time-series data. We hypothesize that this contrast between no-volume flow in karst passageways during dry periods and partial- or saturated-volume flow during a rain event is detectable by these geophysical nodes.

Summary of Accomplishments:
Through literature and field investigations, we have reviewed and examined many of the surface features indicating karstic geology. We developed a list of site criteria for our hydrogeophysical investigations and have begun instrumenting and characterizing a particular site. We are also becoming familiar with Elmer finite element code for developing coupled hydrological and geophysical models for survey design and site characterization.

Significance:
The development of methodologies to characterize semiarid karst hydrology will augment Sandia's mission to lead efforts in energy technologies, waste disposal, and climate security by helping to identify safe and secure regions and those that are at risk. The national, economic, and energy security of the US is reliant on locating and characterizing suitable locations for energy production and waste disposal. The DOE is committed to promoting "scientific and technological innovation in support of that mission." Karst is a common geological feature; in many places, pollutants from municipal and agricultural waste have reached crucial water supplies via karst. The DHS's interest in national security preparedness also depends on improved characterization methodologies; waters are highly vulnerable to intentional

introduction of biological/chemical substances into karst recharge points. The Environmental Protection Agency is similarly committed to the security of water systems.

Surface Electrochemistry of Perovskite Fuel-Cell Cathodes Understood In-Operando
158702

Year 1 of 3
Principal Investigator: F. El Gabaly Marquez

Project Purpose:
Solid-oxide fuel cells (SOFC) are electrochemical devices that convert fuels into electricity at efficiencies greatly exceeding combustion-based technologies. Operated in reverse as solid oxide electrolyzer cells (SOEC), renewable electricity can be converted into carbon-neutral fuels by reduction of water or carbon dioxide. Thus, it is widely anticipated that fuel cells and electrolyzers will be used for storing and interconverting energy at large scales. Key to improving SOFC technologies is eliminating the kinetic bottleneck of the oxygen reduction reaction (ORR), which occurs on the cathode. The chemical state of the cathode surface critically controls the rates of surface reactions and solid-state transport. Unfortunately, the surfaces of perovskite-structured oxides, the state-of-the-art cathode materials, are extremely complex. Thus, developing new approaches to determine the surface chemical states during actual operation is extremely desirable.

This project represents basic research inspired to understand an important longstanding energy issue — how do SOFC cathodes function at an atomic level? The innovation that makes this approach unique is the performance of detailed, quantitative in situ measurements of the surface chemical state while the system is operating. We propose to use in situ electrochemical x-ray photoelectron spectroscopy (EC-XPS) under near-realistic operating conditions of high temperature, gas activity, and in the presence of spatially dependent electric potentials to study the solid-gas interphase of state-of-the-art cathode materials over single-crystal yttria-stabilized zirconia (YSZ). This project will yield new microscopic chemical information about the processes that limit the rates and efficiencies of electrochemical energy storage and conversion. Knowing the chemical states of the surface and of the bulk and the macroscopic response of the electrolyzers/fuel cell (e.g., the current vs. voltage behavior and the impedance spectroscopy) will provide new insights into the complex processes occurring at cathode surfaces. When the combined information is analyzed by continuum models, knowledge about which microscopic processes control device performance will be obtained.

Summary of Accomplishments:
Preliminary in situ measurements of $BaSrCoFeO_3$ perovskite cathodes at the advanced light source have been performed. They yielded relevant information about unexpected segregation of Ba on the surface and show how the La exists only in a unique oxidation state, being probably the cause of its lower (compared to $BaSrCoFeO_3$) catalytic performance. Data is still being analyzed.

Significance:
Understanding the fundamental interactions that govern interfacial electrochemistry will accelerate the pace of innovation for generation and storage of electricity, contributing significantly and beneficially to the nation's and the world's energy future. The fundamental knowledge in electrochemical technology resulting from this project has large importance to the twin challenges of ensuring energy security and mitigating climate change. The goal of enabling efficient, large-scale energy storage and inter-conversion by using solid-oxide fuel cells and electrolyzers is important to the mission of the entire

DOE, including the Office of Energy Efficiency and Renewable Energy, Office of Based Energy Science, and NNSA.

Nuclear Fuel Cycle System Simulation Tool Based on High-Fidelity Component Modeling
158998

Year 1 of 3
Principal Investigator: D. Ames

Project Purpose:
The DOE is currently directing extensive research into developing fuel cycle technologies that will enable the safe, secure, economic, and sustainable expansion of nuclear energy. The path to successfully develop and implement an advanced fuel cycle is highly dependent on the modeling capabilities and simulation tools available for performing useful relevant analysis to assist stakeholders in decision-making. This project therefore will attempt to develop a fuel cycle simulation tool that provides consistent and comprehensive evaluations of advanced fuel cycles, including uncertainty quantification and optimization. In addition, the ability to incorporate policy considerations, environmental impact, and economic projections in the model is planned. The resulting simulator has the unique features of being high fidelity in nature and capable of performing uncertainty analysis and optimization.

Current DOE fuel cycle simulation tools are large-scale system dynamics models that track material flow throughout the fuel cycle at the isotopic level and include decision-making capabilities. The design and nature of these code systems limit the level of detail achievable for reactor simulation and restrict their use for uncertainty analysis applications. Therefore, there is a need to provide a greater level of detail (high-fidelity) component modeling and the capability to perform uncertainty quantification. Such a tool could be used standalone or in conjunction with current fuel cycle analysis tools to provide a complete set of fuel cycle evaluation data to guide decision makers. The project is aimed at filling a gap in the performance of current fuel cycle simulation tools by incorporating whole-core 3D exact geometry reactor physics models that account for specific reactor designs, variations in design parameters, and quantifying the impact on the overall fuel cycle system. A new method and analysis approach will be developed and implemented to overcoming limitations imposed by computational cost that significantly restricts the ability to perform complete analysis of the system, particularly uncertainty quantification and optimization.

Summary of Accomplishments:
In approximately two months of operation the accomplishments include the acquisition of necessary computational hardware and software to successfully meet project milestones and goals. A high performance multiprocessor workstation and software package (MCNPX [Monte Carlo N-Particle eXtended], MatLab, Simulink, SCALE, ORIGEN, and Visio) has been procured and built for optimum computational efficiency. It was determined that this particular platform best fit the high computational demands of the project and was within project budget. A written document specifying the details of the software management plan and the software requirements is complete. The layout of the fuel cycle components has been developed and modeling techniques are being analyzed for the individual components and reactor system models. The project is on schedule to accomplish all FY 2012 goals and within the proposed budget limit.

Significance:
The completion of this study would lead to improved understanding of nuclear fuel cycles and the interdependence of the components and reactors that compose these complex systems. As DOE pursues advanced nuclear systems the need for such information is crucial. This simulation tool would be an

important component in the effort to implement an advanced fuel cycle that best realizes the DOE goals of providing a safe, secure, and sustainable energy source that helps to meet future demand, without creating outside dependencies and has minimal impact on the environment.

Development of a System Model for a Small Modular Reactor Operating with a S-CO_2 Cycle on a DoD Installation that Utilizes a Smart/Micro-Grid
158999

Year 1 of 3
Principal Investigator: T. G. Lewis

Project Purpose:
We will develop a system model capable of simulating the impact of a load varying smart/microgrid on a small modular reactor (SMR) and vice versa for military energy needs. Results of this system model will benefit the selection of SMRs and smart/microgrid technologies. The military is actively seeking technologies capable of delivering energy security. Sandia is currently helping the DoD in investigations related to microgrid for DoD bases, while working on DOE projects targeting the use of domestic SMR technology. It is evident that a SMR operating on a DoD base utilizing smart/microgrid technology could help meet the DoD priority of an alternative secure energy source that can function without the commercial grid.

The application of a dedicated nuclear power system on a DoD installation has been proposed by those who are either in charge of DoD energy security and those who are proponents of nuclear energy, but neither party has investigated how to couple the requirements of the DoD and the rigidity of nuclear power systems operation constraints. Additionally, there is a focus of using advance reactors due to their operations benefits and advanced power conversions systems, but neither technology has been rigorously investigated in terms of applicability to DoD facilities and microgrids. We are pursuing the idea that using a system engineering approach focused on designing a robust-in-scope model to allow for temporal changes to a microgrid behavior, while maintaining a high fidelity with respect to a nuclear reactor's behavior, will produce a system that best fits the unique needs and challenges for a DoD nuclear powered installation. Such a model can be coupled to experimental power systems and computational reactor models. The combination of synthetic grid disruptions and usage patterns will further increase the significance of system performance.

Summary of Accomplishments:
The accomplishments of this project are as follows: development of model physics, determination of model boundary conditions, and preliminary MCNP (Monte Carlo N-Particle Transport Code) based reactor system scoping. Development of model physics relates currently to a sodium coolant to fuel reactivity feedback mechanisms, boundary conditions relates to microgrid component time scales, MCNP relates to the use of MCNPX (Monte Carlo N-Particle eXtended) model of an AP1000 system.

Significance:
The completion of this project will provide the foundation to test advanced nuclear plants in conjunction with critical infrastructure for the DoD and DHS. The applicability of advanced nuclear power systems capable of working in combination with current infrastructure and unique load environments is expandable to civilian population critical needs such as medical facilities and regional government needs after natural or manmade disasters. The use of S-CO_2 Brayton systems improves thermal efficiencies and minimizes size of the power system, making it possible for rapid deployment or evacuation.

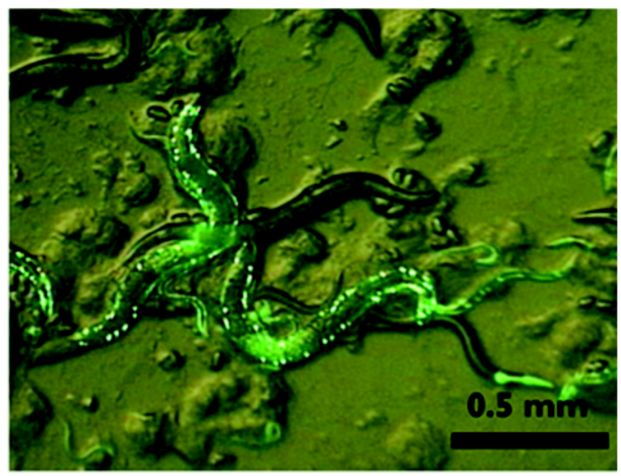
INTERNATIONAL, HOMELAND, AND NUCLEAR SECURITY INVESTMENT AREA

This investment area funds research into a variety of efforts designed to mitigate the risk posed by chemical, biological, radiologic, and nuclear threats against domestic, international, and military populations, as well as threats posed by nuclear and biological proliferation. Through the effective use of science, technology, and full-spectrum system solutions, projects are aimed at providing integrated and sustainable solutions to high-consequence threats, through system design, technology development, and deployment across the threat spectrum — from anticipate to prevent, identify, respond, and recover. By leveraging Sandia's technologies, engineering, and systems integration competencies to engage in global nuclear risk reduction, the investment area seeks to foster interagency and international partnerships in nuclear security, nonproliferation and arms control. Aviation and border security and the ST&E necessary to support these initiatives also fall within the purview of this investment area.

A *C. elegans*-Based Foam for Rapid On-Site Detection of Residual Live Virus

Project 130755

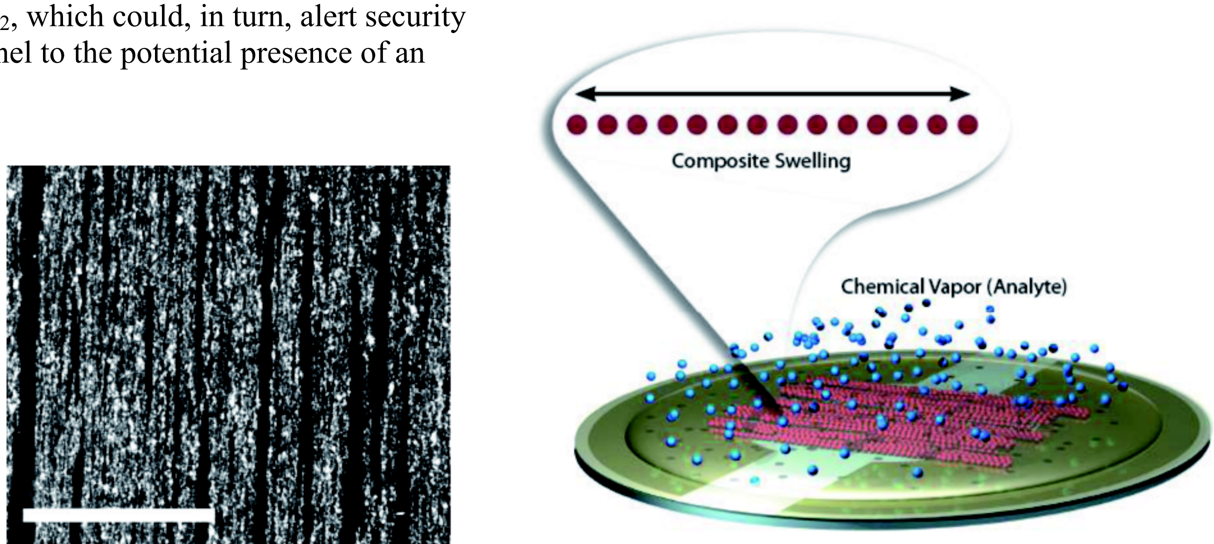
Clearance sampling is a process that occurs in the aftermath of decontamination of a deliberate or accidental release of biological contamination (most often bacteria and/or viruses). Once decontaminated, a site must then be tested for the presence of residual biological contamination to ensure the success of decontamination. This process should occur rapidly and with statistical certainty, but current procedures are time consuming and labor intensive, requiring testing by off-site laboratories. This project has developed a foam derived from the nematode, *C. elegans* that can be applied directly to an entire contaminated area for quick and accurate detection of residual live virus by means of a fluorescent signal, to accomplish clearance detection rapidly and on-site. The project identified nematode strains more susceptible to viral infection, developed a protocol to facilitate viral infection of the nematodes, and generated nematodes expressing viral receptors not normally present in the worms that express a fluorescent protein enabling visualization of viral presence.



Nematodes fluoresce, indicating a reaction to the presence of virus.

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives
Project 149568

Readily made from common household automotive items such as hair bleach and battery acid, homemade explosives (HMEs) present an emerging threat to both US military forces and civilians. In the Middle East, where the supply of munitions from previous conflicts has more-or-less dried up, terrorists are progressively turning their attention toward improvised explosive devices (IEDs) with an energetic-material component derived from commonly available household agents, most notably hair bleach, fingernail polish, and automotive battery acids. Exemplary is triacetone triperoxide, a dangerously unstable homemade explosive that was used as an explosive initiator by British shoe-bomber Richard Reid, and whose synthesis requires the reaction of H_2O_2 (hydrogen peroxide) with acetone in a sulfuric acid medium. More importantly, there is no currently field-deployed technology to detect such HMEs, and therefore, this project's work with portable sensors — polymer-based devices known as field-structured chemiresistors (FSCRs) — is directly aligned with Sandia's national security mission in threat detection. FSCR research examines several schemes for field-detection of the presence of H_2O_2, which could, in turn, alert security personnel to the potential presence of an HME.



Polymeric matrix (micrograph, left, bar = 3 mm) and schematic drawing during swelling upon binding analyte (right), that could serve as chemiresistor detectors of homemade explosives. Upon binding a relevant analyte the polymer swells with a separation of its components and an increase in its resistivity.

International, Homeland, and Nuclear Security Investment Area

A *C. elegans*-Based Foam for Rapid On-Site Detection of Residual Live Virus 130755

Year 3 of 3
Principal Investigator: G. Chirica

Project Purpose:
In the response to and recovery from a critical homeland security event involving deliberate or accidental release of biological agents, initial decontamination efforts are necessarily followed by tests for the presence of residual live virus or bacteria. Such "clearance sampling" should be rapid and accurate, to inform decision makers as they take appropriate action to ensure the safety of the public and of operational personnel. However, the current protocol for clearance sampling is extremely time-intensive and costly and requires significant amounts of laboratory space and capacity ("Method Detection Limits and Non-Detects in the World of Microbiology," National Risk Management Research Laboratory, Environmental Protection Agency [EPA], 2006). Large numbers of samples may be required to achieve a high degree of statistical certainty, depending upon the physical dimensions of the contaminated area. The samples must then be transported to the lab for measurement of biological activity. Detection of residual live virus is particularly problematic and time-consuming, as it requires evaluation of replication potential within a eukaryotic host such as chicken embryos. The purpose of this project was to improve clearance sampling by leveraging Sandia's expertise in the biological and material sciences in order to create a *C. elegans*-based foam that can be applied directly to the entire contaminated area for quick and accurate detection of any and all residual live virus by means of a fluorescent signal.

Summary of Accomplishments:
We achieved the following project objectives: 1) isolation of *C. elegans* with increased susceptibility to viral infection, 2) production of molecular sensors of viral infection, and 3) construction of a mechanism to amplify a fluorescent signal indicative of viral infection. In addition, we have initiated work towards a fourth critical milestone, the production of gels with which to disperse our engineered strains of *C. elegans* on a surface for the purpose of clearance sampling. Towards production of *C. elegans* strains with increased susceptibility to viral infection, we have: 1) identified strains with cuticle defects that are more susceptible to viral infection than wild-type strains, 2) developed a protocol utilizing chemical (chitinase/collagenase) and pressure (10 Kpsi [pounds per square inch]) treatments to facilitate viral infection of *C. elegans*, 3) generated *C. elegans* strains expressing exogenous viral receptors enabling infections not normally possible due to a lack of appropriate cellular receptors, and 4) generated recombinant viruses expressing the red fluorescent protein mCherry, enabling visualization of viral infection in both intact *C. elegans* and mammalian and *C. elegans* cell lines. In addition, we have attempted to generate molecular sensors of for both Rift Valley Fever Virus (RVFV, an ribonucleic acid [RNA] virus), and Vaccinia Virus ([VacV], a DNA poxvirus). We have generated and tested several different sensors of RVFV infection but, in all cases, unacceptably high background expression from the sensor has been observed, with only modest increases in fluorescence observed following infection with RVFV (MP12 strain). By contrast, we have had much more promising results in production of a molecular sensor for VacV infection. We are currently generating and testing different molecular sensors for VacV infection. For one type of sensor, we have used a VacV-specific promoter to drive mCherry expression only in cells infected with VacV.

Significance:

The critical need for improved methods of clearance sampling applicable to all types of biological agents has been emphasized by DHS and EPA in workshop settings. Our proposed technology for clearance sampling would be substantially faster and cheaper than state-of-the-art culture-based techniques, and addresses multiple mission elements by facilitating response and recovery efforts following biological attacks on US interests here and abroad.

Uncooperative Biometric Identification at a Distance
130764

Year 3 of 3
Principal Investigator: K. R. Dixon

Project Purpose:
One of the greatest challenges facing the security of public facilities and infrastructure is the rapid identification and verification of persons of interest. The problem becomes especially acute when considering that some subjects have a motivation to be deceptive or otherwise uncooperative toward identification. Some domains require a high degree of accuracy, such as granting access to a secured building or sensitive area for Force Protection or Virtual Presence and Extended Defense applications. Other domains require high throughput and recognition at a distance, such as the Department of Homeland Security's Transportation Safety Administration airport screening, Immigration and Customs Enforcement's passport control, and monitoring persons around high-value facilities such as the Capitol and the White House. This project aims to create a high-accuracy, high-throughput biometric identification system that works with both cooperative and uncooperative subjects at multi-meter distances.

The human iris is one of the most promising avenues for biometric identification for several reasons. First, the iris is believed to be one of the most stable, unique biometric measurements throughout the course of an adult's life; the iris does not change as a subject ages and is extremely difficult to alter. The project explores new research and development, combining Sandia's expertise in adaptive optics with state-of-the-art research at Carnegie Mellon University in iris identification and facial-pose correction algorithms. The integrated system provides high-accuracy, high-throughput, multi-meter distance iris recognition of both cooperative and uncooperative subjects. We worked closely with Sandia's Force Protection groups to validate the performance of the proposed system with human-subjects data and to verify its capabilities in mission-relevant scenarios.

Summary of Accomplishments:
Our project brought together Sandia's expertise in adaptive optics hardware with university partners in face tracking and multi-spectral imaging and with commercial-off-the-shelf iris recognition technology to create a system capable of identifying semi-cooperative subjects from >30 meter distances in an outdoor setting. During the course of the project, we used first-principles physics to determine that long-range outdoor iris recognition will be dominated by atmospheric turbulence. The integration of adaptive optics with cutting-edge face tracking and control algorithms allowed us to demonstrate our capability.

Significance:
The project ties to the DOE mission of "the development and deployment of technologies to replace costly and manpower-intensive physical protection strategies" and can be used to secure sensitive facilities with a standoff biometric identification of potential threats. The research addresses an acute need of the DHS to create a high-volume biometric identification system to protect public infrastructure and ensure continued public confidence.

Refereed Communications:
J. Choi, K.R. Dixon, D.V. Wick, B.E. Bagwell, G.H. Soehnel, and B. Clark, "Iris Imaging System with Adaptive Optical Elements," to be published in the *Journal of Electronic Imaging*.

Development of Coherent Germanium Neutrino Technology (CoGeNT) for Reactor Safeguards
141616

Year 2 of 3
Principal Investigator: B. Cabrera-Palmer

Project Purpose:
Antineutrinos are extremely penetrating elementary particles that have unique features of interest for safeguards at nuclear reactors: they cannot be shielded, are inextricably linked with the fission process, and provide direct real-time measurements of the operational status, power and fissile content of reactor cores using equipment that is independent of reactor operation. Based largely on work performed by Sandia and Lawrence Livermore National Laboratory (LLNL), the International Atomic Energy Agency (IAEA) Novel Technologies Division has identified antineutrino detection as a "highly promising technology for safeguards applications" at nuclear reactors. Furthermore, the IAEA has suggested that "antineutrino detectors may have particular advantages for the safeguarding of particular reactor types," such as pebble bed modular reactors (PBMRs). However, the IAEA has expressed concerns over the size of current antineutrino detectors (~3 m x 3 m x 4 m) and their use of hazardous materials.

We propose a new antineutrino detector that is much smaller and safer and, therefore, more likely to find widespread acceptance as a monitoring tool. This novel detector would be based on high-purity germanium (HPGe) detector technology, which has been widely used for gamma-ray spectroscopy (including by the nuclear power industry). Our goal is to create a new type of electronic readout system for an HPGe detector that will enable it to be sensitive to an as-yet undetected antineutrino signature — the coherent neutrino-nucleus scattering (CNNS). This process is universally predicted and has a much higher probability of interaction such that a germanium detector of 10 kg would have similar sensitivity to 1 ton of the current scintillator based detection technology. This would allow a significant reduction in the necessary scale for a complete detector system. If successful, this project would lead to a viable technology for reactor monitoring that could be easily incorporated into the global nuclear safeguards regime.

Summary of Accomplishments:
The 800-g Germanium detector element (BEGe model from Canberra Industries) was removed from the Canberra front-end, where the electronic noise FWHM (Full-Width-at-Half-Maximum) was ~150 eV, and inserted in the low-noise front-end developed at Lawrence Berkeley National Laboratory (LBNL), with the goal to isolate any source of electronic noise intrinsic to the interface of the germanium crystal and the Canberra front-end. The measurements in the LBNL test setup show no change in any noise component, indicating that the noise is arising from the detector element itself. A further test, where the detector was replaced by a higher capacitance capacitor, indicates that the noise is largely capacitive. Thus, the next step is to reduce the capacitance of the detector element by reducing the size of the point contact electrode to ~1mm.

LBNL has fabricated a new Germanium detector element with a 1mm-point contact that exhibits a low capacitance (1pF) and low leakage current (1pA), but it unfortunately has poor charge collection. Although poor charge collection prevents us from using this detector for CNNS detection, we will be able to use it to optimize the noise performance of the front-end. Thus, Sandia is currently building the cryostat to fit this detector and the LBNL electronic front-end. We are in the process of acquiring a new Ge-crystal in order to fabricate a good detector element (with low capacitance, low leakage current, and good charge collection).

Since neutrons are a competing background also creating Ge-nucleus recoils, we are building an anticoincidence- neutron-veto surrounding the Germanium detector. The detection material is plastic scintillator due to its large probability for neutron interactions, read out by special low-background photo-multiplier tubes (PMTs). In parallel, we are developing a digital data acquisition (DAQ) that will easily incorporate the readout modules of the Germanium and each active-shield detector.

Significance:
This project supports Sandia's national security mission by creating a new technology to enable enhanced nuclear safeguards for the Assured Nuclear Future. By creating a new detector technology that will be able to directly monitor and verify the fissile operation of a nuclear power reactor non-intrusively and in real time, we will be able to assist the international safeguards agencies in supporting the safe and secure expansion of nuclear energy. There is a growing interest in the global safeguards community for the development of antineutrino detection technologies for reactor monitoring. The Novel Technologies Division of the IAEA has already shown interest in our previous work on antineutrino monitoring of nuclear reactors and in a recent report recognized this technique as a "promising technology for safeguards applications." Currently, our work with scintillator technology is supported by DOE, but they consider the coherent germanium technology to be too far from an applicable technology to support under their existing missions. Other agencies, such as the IAEA have shown interest in the possible advantages that could be provided by a working coherent neutrino detector, but they all await demonstration that the technology is sufficiently mature to warrant developing an applicable detector system.

The successful completion of this project would place Sandia in an advanced leadership position for safeguarding the global future of nuclear energy. Successful demonstration that this technology performs with the desired sensitivities will allow DOE to fund the further deployment and development that would be necessary to demonstrate this technology's true potential for reactor safeguards. With long-term interest from organizations such as the IAEA on the horizon, we foresee the potential for deployment in all future nuclear reactors around the world.

While antineutrino monitoring of a nuclear reactor has already been demonstrated, the IAEA identifies three "technical limitations that prevent immediate incorporation [in the safeguards regime]:
- The toxicity and flammability of (liquid) scintillator materials;
- Shielding against cosmic backgrounds; and
- The physical footprint of the detectors."

The new germanium detector technology directly addresses all of these technical limitations. Cryogenic germanium detectors are already well known and are frequently used at nuclear reactor facilities around the world. Therefore, the technology would have far greater accessibility with few or no safety concerns from the facility operators. In addition, the ability to shrink the active detector from 1 ton of scintillator material to something on the order of 10 kg of germanium would allow much greater flexibility in finding locations suitable for detector installation.

If successful, an important technical output of this project would be the development of a new large-mass germanium detector with unprecedented low noise. First-time observation of neutrino coherent scattering would represent a significant scientific breakthrough.

Safeguards and Arms Control Authentication
141669

Year 2 of 2
Principal Investigator: P. B. Merkle

Project Purpose:
Nuclear disarmament protocols and international safeguards inspections require rapid and confident determinations that equipment and facilities are authentic and free from tampering. Each party must be able to detect counterfeits or facility alterations that might enable treaty subversion. Gloveboxes, structures, and equipment enclosures must be inspected for subtle alterations to assure confidence. Periodic safeguards inspections assure the integrity of structures such as pipe networks and process vessels, since undetected alterations (wall penetrations or hidden ports) may allow material diversion. Inspection to detect tampering of smaller safeguards monitoring equipment such as cabinets, housings, and communications conduit is necessary to ensure data authenticity, create cost savings from equipment joint use, and deter undeclared activities. We proposed to investigate and develop a flash thermographic signal reconstruction (TSR) inspection technology to detect alterations in equipment and structures used for safeguards and arms control. We researched and developed field-ready methods and materials for coating surfaces to establish the authenticity of equipment and structures. This research provides a unique and widely applicable solution for NNSA, Defense Threat Reduction Agency (DTRA), Department of State, and the International Atomic Energy Agency (IAEA) programs to address known shortfalls in facility and equipment authentication capabilities. We delineated the performance of high resolution flash (or “pulsed”) thermography on artfully tampered structures and items, evaluated surface coating methods and materials for field detection enhancement, and developed the technology to the point of field evaluation. There is currently no field-ready technology available to rapidly authenticate objects and structures of varying compositions across a wide size range. Creating a broadly applicable method is very challenging, since the materials and surfaces in question vary considerably in complexity, composition, and size.

Summary of Accomplishments:
The system was used to evaluate an assortment of field-usable surface treatments, including commercial adhesive films, paints, and custom-formulated coatings. A translucent contact adhesive film was found to provide the best combination of radiative and application properties, including ease of application and satisfactory defect contrast enhancement. A mock field inspection was conducted with detail scans of floor, wall, and storage container items. We converted the commercial laboratory thermography system into a field-deployable unit and conducted a mock inspection at a field site. This involved ruggedizing the electrical cabling and restacking the components into all-weather shipping crates with wheels suitable for transport on rough ground. An inspector's procedure was developed along with the fabrication of a multipurpose field standard test item. This was a metal plate with two types of defects: 1) a hole that had been plugged and expertly repaired, and 2) a set of rear-wall trenches of varying depth. An inspector or joint monitoring team could verify the instrument performance against this standard for functional testing. We discovered that larger areas with complex structure such as overhead ducts and pipes could be qualitatively scanned at a larger distance than expected, suitable for indicating the presence of gross subsurface defects.

Significance:
The NNSA and DOE mission areas of arms control treaty verification and international nuclear safeguards are supported by the practical development and mock field-testing of this technology. This system, if further integrated into chain of custody and safeguards technical architectures, will comprise a

deterrent to adversaries intent on physical tampering of facilities and equipment. This project has produced a field-ready system to physically authenticate the integrity of many different materials that comprise structures, objects, and security devices that are critical to physical and cyber security. It will provide an additional layer for "defense in depth" for disarmament and fissile material control operations.

Characterizing Pathogens Based on Host Response
141676

Year 2 of 2
Principal Investigator: S. Branda

Project Purpose:
Biological weapons of mass destruction (WMDs) and emerging infectious diseases pose serious and growing threats to our national security. Effective response to an outbreak critically depends upon rapid and accurate characterization of the causative pathogen. Current detection systems focus on notorious pathogens (e.g., anthrax) but are blind to unanticipated pathogens (natural or engineered). This is because they rely upon pre-selected, highly specific affinity reagents (antibodies, polymerase chain reaction [PCR] primers) that recognize physical/chemical features of the pathogen; change or absence of those features can wholly thwart detection. Current systems also provide no information as to the viability and virulence of detected pathogens.

We are developing a system for rapid detection of pathogens and assessment of their virulence capacity, based on characteristic responses that they elicit in immune cells. This system relies upon: 1) exquisitely precise culture and infection of immune cells, to ensure reproducible responses; and 2) capture of responses that are robust and complex enough to support identification of pathogen-specific response signatures. To meet these requirements, we are developing a “digital” microfluidics (DMF) platform that offers unprecedented control over the microenvironment experienced by the cell, as well as capture of the global transcriptional response (i.e., transcriptome) of individual cells. In tandem, we are developing a new information-handling architecture that, via coordination and integration of existing data analysis tools, accelerates and automates identification of pathogen-specific response signatures. Our system will provide response signatures of greater discriminatory power, enabling accurate inference of the pathogen's identity and virulence capacity, based on analysis of its impact on the host cell's transcriptome.

Summary of Accomplishments:
We completed development of a microfluidics-based platform for automated culture, infection, lysis, and ribonucleic acid (RNA) extraction of small populations of mammalian cells. The “Novel Agent Characterization via Microscale Infection Analysis” (NACMIA) platform performs all of its tasks in a fully automated and highly reproducible manner, greatly improving upon benchscale methods for ex vivo infection studies with less burden on labor, less risk of human error, less exposure to infectious agent, and less variability due to smaller cell population size and precise dosing and timing. We demonstrated the approach and its advantages using bacterial particles to challenge mouse macrophages and measuring host transcriptional response by quantitative reverse transcriptase (qRT)-PCR; the experiments were carried out using NACMIA as well as at benchscale for comparison. We found that host responses were similar regardless of approach, and the advantages listed above were confirmed. We are completing a manuscript describing NACMIA and the results of these experiments. We are also completing a manuscript describing host response profiling using Next-Generation Sequencing (NGS) rather than qRT-PCR as the method for analyzing macrophage expression in response to bacterial challenge. In this case, the experiments were carried out at benchscale, and the focus is on identifying pathogen-specific host responses through comparison of expression elicited by wild-type vs. mutant Francisella tularensis. This work is an important contribution to the study of host-pathogen interactions, and knowledge gained from it and follow-on studies will better enable the biodefense and public health communities to effectively detect, identify, characterize, and combat infectious diseases.

Significance:
Biological WMDs and emerging infectious diseases are real and present dangers to this nation. To mount an effective response to a bioweapon attack or disease outbreak, we must understand the causative pathogen and the threat that it poses. Current pathogen detection systems do not recognize unanticipated pathogens (naturally emerging or engineered), nor do they provide information about the pathogen's virulence capacity. By filling this gap, our system represents an important and lasting contribution to homeland defense, supporting the national security missions of DOE and DHS.

Graded Engagement of Small Aircraft and UAVs for Physical Protection
141678

Year 2 of 3
Principal Investigator: J. F. Jones

Project Purpose:
Military nuclear weapon storage areas and NNSA sites are vulnerable to threats posed by small, low flying aircraft such as small fixed wing airplanes, helicopters, and unmanned aerial vehicles. To counter this threat, a system is needed that is able to detect a possible threat, discourage it from proceeding toward the sensitive area, and, if necessary, prevent it from carrying out a nefarious task.

Systems exist for the detection, tracking, warning, and destruction of aircraft. However, systems that can employ a graded engagement approach do not exist, nor does the concept of operations or system architectures to realize a graded engagement approach exist. North American Aerospace Defense Command, Northern Command (NORAD-NORTHCOM) has invested heavily to solve this problem in the national capital region. Major issues remain, and there is wide diversity of opinion on how to approach the problem.

For a graded engagement approach to be realized, several technological gaps must be addressed. Technologies that can project effective, adjustable-level discouragement or deterrence toward a variety of manned and unmanned threats must be identified and matured. Also, capabilities that can neutralize the threat with minimal collateral damage to the surroundings must be identified and matured. Finally, a system architecture is needed that is capable of integrating detection, assessment, response, real-time target effects, and collateral area impacts assessments to guide the graded engagement, all with appropriate human authorization.

We proposed to assess if engaging threat aircraft with less than lethal stimuli could mitigate risk by diverting errant aircraft, deterring aircraft with mischievous intent, or interrupting aircraft with nefarious intent. If successful, we will possess a validated system architecture, technology development roadmap, and strategic partnerships to develop and ultimately deploy an effective system capable of protecting critical facilities against threats posed by small aircraft.

Summary of Accomplishments:
In the first year of the project, we framed the problem by establishing a broad understanding of the problem and constraints including developing simplified abstraction of the process flow and win/loss criteria. We identified system component performance attributes including the battlespace environment, threat aircraft performance, and detection technologies performance. We conducted an extensive literature survey on non-lethal weapon technologies that could be applied to aircraft engagements along with neutralization technologies including anti-aircraft guns and missiles.

In the second year of the project, we demonstrated two innovative technologies and began developing a modeling environment to test our original hypothesis.

One of the innovative technologies is a new radio technology that can simultaneously transmit on a 760 aviation frequencies to rapidly contact an errant pilot tuned to the wrong frequency, which is a typical problem. We envisioned two deployment scenarios and conducted sufficient analysis to demonstrate the feasibility of the technology.

To better understand the implications of engaging aircraft over an urban environment, we developed and demonstrated the capability to project an aircraft's possible future trajectory and overlay that area with critical infrastructure, population densities, etc. This allows us to assess the win/loss criteria investigated in the first year where we discovered that engaging an aircraft could have more severe consequences in an urban environment that if the aircraft were allowed to attack its target. We briefed our results to NORAD-NORTHCOM, who sees great merit in the technology as a situational awareness tool to be used in real time.

Significance:
This project is investigating innovative technologies and methodologies to address threats posed by aircraft being used as improvised weapons against targets in the US. Instead of trying to solve a problem that is too difficult, we are working to make the problem less difficult by approaching the issue differently. Specifically, the US has violations of highly restricted airspace so frequently that it is beyond our capability to determine if all the violations pose a threat. The vast majority of the violations are due to errant pilots. Thus, our approach is to invent new technologies that deter errant pilots, thereby freeing defenders to focus on more likely potential threats.

One of the promising technologies that we have conceived and are working to prove is a new radio technology that can simultaneously transmit on 760 aviation frequencies to rapidly contact an errant pilot who has tuned to the wrong frequency, which is a typical problem.

Capabilities are only useful if they can be employed. To understand whether they can, this research is developing modeling and simulation capabilities that incorporate algorithms to evaluate impacts from decisions of time-based events of an air threat on targeted assets. This capability will enable us to rapidly script scenarios that include a variety of physics-based phenomena (e.g., air vehicles, collections of sensors, deterrent devices, etc.) with operational behaviors. Numerous scenarios can be executed to perform parametric sensitivity studies on system effectiveness and sensitivity. This extension to the UMBRA (modular simulation framework) environment will enable evaluating mission tactics within realistic physical environments with the temporal constraints of the air battlespace. This modeling capability also incorporates geospatial technology to identify assets and critical infrastructure potentially at risk as well as assessing collateral damage potential in real time.

In summary, this project is pioneering new technology and new modeling and simulation capabilities to address a very difficult and pressing issue for NNSA and national security.

Rapid Radiation Biodosimetry to Mitigate Exposure Scenarios
141680

Year 2 of 3
Principal Investigator: G. J. Sommer

Project Purpose:
"Presently available methods are not satisfactory for managing the medical casualties from an R/N (radiation/nuclear) event and there is urgent need to develop new capabilities to assess radiation dose quickly with at least moderate precision." — DHS S&T Technology Assessment and Roadmap for the Emergency Radiation Dose Assessment Program (ERDAP)

Radiological and nuclear incidents continue to threaten the Homeland Security and Defense (HSD) landscape. Sandia systems analyses addressing high-consequence terrorist threats, including Radiological Dispersal Device (RDD) and Improvised Nuclear Device (IND) scenarios, highlight the need for rapid triage and assessment of priority victims and the "worried well" following a radiological event. Responsive therapeutic administration requires dosimetry tools that detect doses of 1-8 Gy (1 Gray = 1 Joule of radiation absorbed per kg tissue) within 24 hours post-exposure for avoidance of long-term health effects and improved survival rates. For mass-exposure scenarios, these tools must be available at the point-of-incident and operate at a rate of 1 assay every 10 minutes. However, state-of-the-art biodosimetry fails to meet these requirements. Current early-response measures (i.e., time-to-onset of vomiting and external emission dosimetry) provide only broad qualitative dose approximations, lacking the sensitivity required for proper therapeutic response. Dr. Blakely's group at the Armed Forces Radiobiology Research Institute (AFRRI) has identified, through exhaustive animal model testing, the changing protein and leukocyte levels in blood within minutes to days following exposure to even low levels (< 1 mGy) of radiation. However, traditional methods for detecting these biomarker fluctuations do not satisfy logistical needs of HSD scenarios. We propose to address this unmet need by: 1) using Sandia's proven microfluidic platform to detect biomarkers for radiation biodosimetry by testing animal model samples in collaboration with Blakely's group, and 2) demonstrating that the portable platform satisfies the need for a rapid, deployable biodosimeter enabling timely and effective therapeutic response even for large population exposure incidents.

Summary of Accomplishments:
This project has driven development of the SpinDx: a novel point-of-care diagnostics platform based on centrifugal sedimentation microfluidics. The simple and versatile design of the platform allows us to achieve multiplexed, parallel immunoassays and white blood cell counts directly from whole blood samples.

Notable FY 2011 technological advances include improving our detection limits to ultrasensitive levels by employing quantum dot detection labels and reducing the fluorescent background signal (~100-fold more sensitive than gold standard enzyme-linked immunosorbent assay [ELISA]). Our reagent conjugation protocols have been optimized, enabling assay testing for new targets with < 1-day turnaround. We have calibration curves for 8 AFRRI radiation-responsive protein markers with dynamic ranges bracketing the clinically relevant concentrations in whole blood. We have also developed novel on-disk routing methods; a single sample can be loaded into an inlet port, and then routed to individual channels for processing. Further, we have improved our fabrication methods such that large batches of disks can be produced in high-throughput with minimal effort by using injection-molding procedures. We have also improved our platform instrumentation such that all disk spinning and analysis steps are pre-programmed and automated. Our custom light-emitting diode (LED)-based fluorescence detector is mounted on linear stages enabling rapid scanning of the channels for automated results output. Finally we have implemented a high-speed industrial camera and strobe to capture on-disk transport and mechanics in real time while spinning.

In July 2011, our AFRRI collaborators conducted an extensive mouse model irradiation experiment, shipping whole blood samples to Sandia for protein and hematology analysis. Results show high correlation with gold standard assays conducted at AFRRI. We anticipate a high-impact publication from this work. This work has generated one peer-reviewed publication (Clinical Chemistry), four manuscripts in-preparation, several international conference presentations, and two patent applications. We will deploy a prototype platform to AFRRI in FY 2012 for a follow-up mouse irradiation verification study.

Significance:
This research will significantly enhance Sandia's capabilities to support current national needs in the response to nuclear or radiological terrorist events. Current DOE- and DHS-funded research at Sandia in these response areas emphasizes threat definition, prevention, and early crisis management. New capabilities in the medical response arena for such events would permit a more comprehensive systems approach to these threats. The research will contribute to the Laboratories' very strong mission addressing RDD scenarios and urban nuclear terrorism. This research will provide new approaches for exposed population triage and assurance of the worried well in such events.

Beyond radiation biodosimetry, this work has resulted in a powerful SpinDx point-of-care diagnostics platform that can be leveraged for many other applications. Our ability to directly analyze complex biological samples such as blood and saliva, as well as complex consumable matrices such as food and environmental samples, gives us key advantages over alternative microfluidic and point-of-care assay techniques. We have obtained exciting proof-of-principle results for assays targeting nucleic acids, toxin diagnostics, bacterial and viral pathogens, and DNA quantitation. This work has opened opportunities for collaboration with several high profile external collaborators to pursue these applications and push the SpinDx towards eventual commercialization and clinical adoption. A radiation biodosimetry platform with multi-use capability (i.e., routinely used in clinical practice but can be easily deployed in a radiation exposure incident) will ultimately be more effective and widely used than a platform dedicated solely to dosimetry.

Refereed Communications:
U.Y. Schaff and G.J. Sommer, “Whole Blood Immunoassay Based on Centrifugal Bead Sedimentation,” *Clinical Chemistry*, vol. 57, pp. 753-761, March 2011.

The Web Sensor: Advanced Analytics for Web-Based Intelligence Analysis
141682

Year 2 of 2
Principal Investigator: R. Colbaugh

Project Purpose:
There is increasing recognition that web data, such as webpage content, dialog between bloggers, and relationship structures in social networking sites represent an important source of information for national security applications. However, making good use of these data is very challenging. While several groups in the government, academic, and commercial sectors have built tools for collecting web data, much less progress has been made to develop the robust, scalable computational analytics required to extract actionable information from this massive, networked, heterogeneous, dynamic, and noisy information environment. An additional challenge is to persuade working analysts that adopting any such new capability will be worth the effort. This project addresses these challenges.

We proposed to create an easily configurable, analytically powerful server-based tool that enables individuals and workgroups to specify classes of phenomena to monitor and investigate via the web. The tool collects three types of data — content (e.g., blog posts), topology (e.g., of hyperlinked documents), and dynamics (e.g., topic evolution) — and encode these data as time series of semantic graphs. We developed a novel process for web analytics which combines content analysis, graph-based topology analysis, and time series analysis in three phases: 1) discover potentially relevant sources of web data (e.g., via focused, adaptive web crawls) and phenomena of interest (e.g., through semantic graph-based anomaly detection), 2) characterize each domain (e.g., identify influentials, quantify authoritativeness, infer sentiment), and 3) perform situational awareness and warning (SAW) analysis (e.g., via our new predictive analysis methodology). A collaborative environment has been designed to support rapid assessment of and interaction with the information being generated by the advanced analytics. Finally, as a first step to persuading analysts of the potential value of Web Sensor capabilities, the tool will be applied to two real world national security problems (nuclear installation threat alerting and extremism SAW).

Summary of Accomplishments:
- Developed a methodology for security-relevant Web-based discovery, situational awareness, and prediction.
- Developed/demonstrated/tested:
- data discovery/assessment/summarization tool;
- individual content/topology/dynamics analysis methods that outperform state-of-art for Web;
- combined content/topology/dynamics methods that outperform individual techniques and provide fundamentally new capabilities).

Produced numerous S&T and applied results (e.g., ~20 papers including Institute of Electrical and Electronics Engineers (IEEE) Intelligence and Security Informatics (ISI) Best Paper and Knowledge, Discovery and Data Mining (KDD) Keynote, four software packages) and attracted new customers (State, DARPA).

Significance:
Growing interest and vast potential exist for Web analytics, but critical challenges remain, including (scale, dynamics, noisy/heterogeneous data, and R&D foundations). This project addresses these challenges directly, so success means differentiating, strategically important capabilities for Sandia. The

Web Sensor has the potential to significantly impact DOE and national security missions. The project should directly impact to DOE's NNSA mission through the main case study and infrastructure security activities by developing threat discovery and warning capabilities that are applicable to such systems. Additionally, we expect the Web Sensor to be directly relevant to missions at DHS, (e.g., via the extremism/radicalization case study), and DoD in areas such as influence operations, counterterrorism, and cyber-security. It is anticipated that Web Sensor capabilities will be applicable to other areas as well, (e.g., human health with the Department of Veterans Affairs).

Refereed Communications:

K. Glass and R. Colbaugh, "Web Analytics for Security Informatics," Proceedings of the IEEE European Intelligence and Security Informatics, Athens, Greece, September 2011.

R. Colbaugh, "Counter-Radicalization and Social Networks: What do the Data Say?" Proceedings 2010 INFORMS Annual Meeting, Austin, TX, November 2010.

R. Colbaugh and K. Glass, "Detecting Emerging Topics and Trends via Predictive Analysis of 'Meme' Dynamics," Proceedings of the 2011 AAAI Spring Symposium Series, Palo Alto, CA, March 2011.

R. Colbaugh, "Predictability of Social Dynamics: An Appraisal," Proceedings of the 2011 SIAM Conference on Dynamical Systems, Snowbird, UT, May 2011.

M. Planck, K. Glass, I. Lyman, and R. Colbaugh, "A Framework for Near Real-Time Event Characterization within the Internet," Proceedings of the IEEE International Workshop on Network Science, West Point, NY, June 2011.

R. Colbaugh and K. Glass, "Proactive Defense for Evolving Cyber Threats," Proceedings of the IEEE International Conference on Intelligence and Security Informatics, Beijing, China, July 2011.

R. Colbaugh and K. Glass, "Agile Sentiment Analysis of Social Media Content for Security Informatics Applications," Proceedings of the IEEE EISI Conference, Athens, Greece, September 2011.

R. Colbaugh, K. Glass, and G. Willard, "Vulnerability Analysis for Complex Networks Using Aggressive Abstraction," to be published in the *Journal of Intelligence Community Research and Development*.

K. Glass and R. Colbaugh, "Estimating the Sentiment of Social Media Content for Security Informatics Applications," to be published in *Security Informatics*.

R. Colbaugh, and K. Glass, "Proactive Cyber Defense," Chapter to be published in Springer Integrated Series on Intelligent Systems.

R. Colbaugh, and K. Glass, "Exploiting Meso-Scale Social Network Dynamics for Predictive Analysis," to be published in *Security Informatics*.

Modeling a Chemical Defense Strategy
148373

Year 2 of 3
Principal Investigator: T. M. Hoette

Project Purpose:
Despite the long history of use of chemical weapons and repeated indications that terrorist groups possess both the ability and intent to employ chemical agents, surprisingly little attention has been focused on developing defensive concepts, much less a comprehensive strategy for civilian chemical defense. The objective of this project is to develop a comprehensive model of chemical terrorism events to enable the clear delineation of which phases of the attack cycle provide optimal opportunities for intervention, what strategies offer the most promise of preventing or mitigating these attacks, and where significant gaps exist in our capabilities to prevent, detect, or respond to a potential attack.

The main product of this project is a top-down systems model of civilian chemical defense developed through the methodologies of Complex Adaptive Systems of Systems (CASoS) Engineering. Given the wide diversity in defense architecture components and the need for flexibility in the face of an ever-evolving threat, we argue that an effective defense structure will exhibit the hallmark features of a CASoS: emergent behavior, self-organization, and adaptability.

Defending against chemical attack is unique compared to defending against other Weapons of Mass Destruction (WMD) in two ways: 1) the potential for dual use of industrial chemicals as weapons, and 2) the comparatively short toxic time-to-effect of chemical agents. As a result, general WMD defensive strategies may be ineffective for chemical defense or have cascading impacts that result in no net benefit to the nation. The overall effectiveness of defensive measures can only be observed with an end-to-end perspective of the entire chemical defense system. We hypothesize that a top-level chemical defense model developed based on CASoS engineering is the most effective approach to account for these parameters. The creation of this systems model will: 1) contribute to the methodology development of CASoS, and 2) provide a tool to improve our approach to chemical defense.

Summary of Accomplishments:
An analysis framework has been developed for the chemical defense system. The structure of the framework is an integrated flow diagram that incorporates all the defense and adversary activities and interactions involved in the chemical attack cycle. Collaborative conceptual modeling and representation were employed to develop the framework. The framework is designed to be modular so that a subset of the system can be studied individually, (e.g., the chemical release and exposure), but still within the context of the overall system. This framework has been vetted both internally with other Sandia systems analysts and externally with government agencies. Several analysis tools have been identified and are being incorporated into the overall CASoS model. Many of these tools are now being utilized to model the dynamic interactions within the chemical defense system, to identify knowledge gaps in our approaches to defense, and to performing high-level trade studies within the context of the overall framework.

In order to explore the behavior of the chemical defense system, a top-level system dynamics (SD) model was developed. In particular, the SD model explores the dynamics involved in how perceived needs are developed into capabilities for both the adversary and the defense. In addition to the SD model, a network-based game theoretic model is under development to evaluate the antagonistic interactions and iterative decision-making of an adversary and a defense. The model is currently based on an airport defense scenario; however, the analysis methods could be applied to many types of chemical defense scenarios. The scenario information determined in the game-theory model can be used as input to configure consequence models, (e.g., hazardous declaration [HazDAC]). Finally, using an agent-based exposure model such as HazDAC, enhanced response architectures for mitigation of public health consequences can be assessed.

Significance:

Chemical terrorism, both at home and against US interests abroad, continues to be viewed as a significant risk at the highest levels of government. Sandia is a national security lab seeking to provide full systems solutions to complex problems. This project will provide a comprehensive systems model of chemical terrorism events that will permit optimization of chemical defenses via insights gained by examining various overall defensive postures. Currently within DHS there are multiple parallel efforts to develop chemical defense resources and capabilities. However, the integration of these defenses into an end-to-end chemical defense architecture is still needed. The chemical defense model developed in this project has already and will continue to be the platform on which Sandia will support government agencies in their efforts to develop an integrated, cohesive defense strategy. This project will specifically benefit programs funded by DOE, DHS programs funded by DHS/CSAC (Chemical Security Analysis Center), DHS/OHA (Office of Health Affairs), and DHS/S&T, and programs funded by DoD/DTRA (Defense Threat Reduction Agency) and DoD/OSD (Office of the Secretary of Defense).

Development of Chemiresponsive Sensors for Detection of Common Homemade Explosives
149568

Year 2 of 3
Principal Investigator: C. M. Brotherton

Project Purpose:
One of the newest terrorist threats to both the public and the military is referred to as homemade explosives (HMEs). HMEs can be synthesized using commonly available chemicals, and among the most dangerous new threats are HMEs made with peroxides. Peroxide-based HMEs are particularly dangerous because there are few viable detection methods that can identify them. This project will focus on developing a new sensor capable of detecting peroxide-based HMEs. The sensor technology of interest is a polymeric chemiresponse sensor first developed at Sandia. The sensor consists of aligned conductive particles embedded in a polymer monolith. Upon exposure of the monolith to the analyte, the polymer swells, thereby causing the embedded particles to separate and produce a change in conductivity. Previous work using the baseline technology focused on detecting contamination of water by organic solvents. This project expands the capability of this sensor approach by developing new polymeric materials that are sensitive to peroxides. This will be achieved by investigating different embedded particle types, sizes, and configurations and by studying and understanding the kinetic response of the polymeric materials to analytes in the gas phase. At the conclusion of this project, a sensor design will be identified that will be able to sense peroxides in the gas phase.

Summary of Accomplishments:
Progress has been made in developing and deploying a sensor testing capability, producing new sensors with increased sensor sensitivity, and developing a peroxide sensitive material for use in a peroxide-based homemade explosive sensor. Typically, the chemiresistors under investigation are not sensitive to polar molecules, such as hydrogen peroxide or water. We have identified six different materials that are expected to interact with hydrogen peroxide. Experiments were performed to determine how to incorporate the six identified materials into a polymer matrix of polydimethylsiloxane (PDMS) and produce a stable polymer. The experiments included Fourier transform infrared spectroscopy, gel point determination, polymerization kinetics measurements, and x-ray fluorescence spectroscopy. Using these techniques, formulation composition, catalyst concentration, and reaction procedures have been developed to produce solid polymers with the appropriate physical and chemical characteristics. Of the six candidate materials, one has demonstrated sensitivity to hydrogen peroxide and has been incorporated in a chemiresistor capable of detecting hydrogen peroxide vapor. Future work will focus on optimizing the sensor to increase sensitivity and decrease reaction time. Additional work will also investigate the susceptibility of these hydrogen peroxide sensors to commonly encountered interferents.

Significance:
The development of biaxially aligned magnetic particle/polymer composites as sensor elements aligns with DOE goals for scientific discovery and innovation. Improved sensor technologies and new approaches to the identification of terrorist materials will benefit DHS and DoD.

Extending Algorithms for Pattern Detection in Massive Data Sets to Commodity Cloud Platforms
151312

Year 1 of 2
Principal Investigator: T. Plantenga

Project Purpose:
The goal of this project is to develop advanced algorithms for use in mining data stored in commodity clouds. The work builds on specific Sandia expertise to address DHS applications.

Massive amounts of data (terabytes to petabytes) are currently collected in many applications of significance to DHS, including cyber network defense, biological sensors, and border security. Analysts need tools that can process huge volumes of data to find interesting patterns and anomalies. The project focuses on two advanced algorithms: tensor decomposition methods and inexact subgraph isomorphism matching. Both algorithms are in expanding areas of research where Sandia is already a recognized world leader.

The novel feature of this project is the expansion of these algorithms into commodity cloud computing environments, where massive data sets are increasingly likely to be located. Commodity clouds are relatively cheap, highly scalable in terms of data storage, and may provide the only storage option for certain business cases. The project targets Hadoop MapReduce, a popular distributed computing paradigm for commercial clouds (Amazon, Google), and clusters of dedicated PCs.

The primary innovation is to extend tensor decomposition methods and inexact subgraph isomorphism matching to the commodity cloud environment. Current implementations of these algorithms are for single workstations or large shared memory machines. They are not practical for massive data sets acquired and stored in distributed memory clouds.

A second innovation is to formulate data mining applications as mathematical models that can be addressed by the two anomaly finding algorithms. Example models exist, but DHS applications considered for this project differ substantially from studies found in the literature.

Summary of Accomplishments:
In FY 2011, the project had three major accomplishments: 1) a scalable MapReduce implementation of inexact subgraph isomorphism matching, 2) successful anomaly detection from terabytes of network defense data, and 3) tools and techniques for testing and improving MapReduce algorithm performance.

1. The subgraph isomorphism code was proven to be highly scalable on a 64-node Hadoop cluster. In one test it found 800 matches from a graph of 83 billion edges, processing over 30 terabytes of intermediate data. The code was modularized to isolate the core algorithm from data, making it easy to adapt to different applications. The software was successfully ported to a collaborator. A paper on this work will be submitted soon.

2. A cyber defense application was addressed in FY 2011. Several terabytes of authentic network defense data were acquired, cleaned, and examined. MapReduce jobs were written to characterize the data in novel ways, which guided the search for anomalies. Suspicious web redirect patterns were found using subgraph isomorphism at terabyte scale. Unusual web search patterns were formulated as tensor decomposition problems, leading to detection of anomalous user behavior. The

tensor computation dealt with only megabytes of data that remained after MapReduce preprocessing and filtering of the terabyte data set. Anomalies from both algorithms were verified by network defense experts within and external to Sandia.

3. The project developed parsing and visualization tools to show performance details of MapReduce jobs. Hadoop tuning parameters were investigated and documented. The project extended research from another project, generating and testing large-scale power law graphs. The test graphs became benchmarks in this project for improving performance, leading to a novel partitioning technique that proved useful to an external customer.

Significance:
The project had immediate value for two collaborators with applications in cyber network defense. A form of the subgraph isomorphism software was ported to a collaborator. The algorithm was adapted to a particular version of Hadoop, and the software will likely be used on practical problems in the near future. A second collaborator, the DHS National Cyber Security Division's (NCSD) Einstein Program, benefited from MapReduce experience with cyber data acquired during the project.

Looking to the future, the anomaly detection methods developed in FY 2011 can be used in other application areas with massive data sets. FY 2012 will focus on a new application in biodefense, the RaPTOR project for detecting biological anomalies. Other security mission areas of interest include physical security (anomaly detection from secure perimeter sensors), and radiation detection for US Customs and Border Protection. There are two steps in applying MapReduce algorithms to a new area: formulation of the problem in appropriate mathematical terms, and collection of data in a Hadoop distributed file system. FY 2011 provided experience in both steps that will make it easier to take on new applications.

The FY 2011 development of a scalable MapReduce implementation for subgraph isomorphism matching will prove useful to applications that search for anomalies. Besides anomaly detection, subgraph isomorphism matching has been used in the literature to help find genetic sequence motifs, evaluate queries made to semantic databases, and characterize the structure of network graphs. The software from this project is easily adapted to different applications, and allows problems of unprecedented scale to be addressed.

The past year indicates more collaborators within and outside Sandia are considering the processing of massive data sets through cloud computing. The open source Hadoop software framework chosen for implementation has become the dominant player in “Big Data” projects for government and commercial entities. FY 2011 accomplishments helped establish Hadoop MapReduce as an area of expertise for Sandia, which should be helpful in many future projects. Framework configuration options were explored, performance analyzed, and Hadoop software variations examined.

Using Fast Neutron Signatures for Improved UF_6 Cylinder Enrichment Measurements
151315

Year 1 of 3
Principal Investigator: S. Kiff

Project Purpose:
One of the most important problems in nonproliferation is monitoring the degree of enrichment from uranium enrichment plants. Centrifuge enrichment plants are necessary to produce fuel for commercial power plants but are also capable of producing highly enriched uranium, which can be configured into a nuclear weapon. Existing technologies for measuring U-235 enrichment in a UF_6 cylinder require controlled conditions for accurate measurements, making them susceptible to diversion scenarios. One significant scenario relates to the UF_6 distribution within a cylinder, which varies depending upon the filling and storage conditions. Low-energy neutrons and gammas used by current technologies have short penetration through dense UF_6, and since the UF_6 thickness near the measurement location is not known a priori, the current measurement techniques are insensitive to UF_6 in the center of the detector. Thermal neutron counting rate near a cylinder can vary by as much as 50%, depending upon the solidified geometry and the cylinder orientation relative to the detectors.

Our project is to apply fast neutron spectrometry and imaging to ascertain the UF_6 enrichment inside the cylinder. Deeply penetrating fast neutrons allow measurements that are sensitive to materials throughout the entire cylinder. Imaging the UF_6 material distribution within the cylinder allows compensation of geometry-dependent measurements when the UF_6 mass is unevenly distributed.

This proposed UF_6 cylinder imager is unlike any other enrichment monitor: neither neutron spectrometry nor fast neutron imaging has been applied to UF_6 cylinder enrichment measurements. Technical risks are that the neutron spectrum may degrade via scattering such that spectrometry becomes impossible; also, the benefits of imaging are unknown at this time. If successful, this project will produce an enrichment measurement technique that is more accurate and more sensitive to diversion scenarios than current technologies. This project proposes to determine the merits of neutron imaging in this application.

Summary of Accomplishments:
To date in FY 2011, progress has been made on three parallel efforts.

1. Detailed simulations of the expected UF_6 neutron emissions in a 30 B cylinder have been modeled using MCNP5. A study of possible spectral degradation mechanisms, such as scattering in the UF_6 and induced fission, concluded that the measurement technique is still likely to work. Also, simulations have been run using three uranium enrichment scenarios: natural, depleted, and 5% enriched U. The modeled system response appears to be a monotonic function of enrichment in this regime, further indicating that spectrometry will be useful for enrichment measurement.

2. In the laboratory, experiments are currently under way to improve the understanding of our spectrometry systemôs performance at energies near the threshold (around 1 MeV). The system uses liquid scintillation as a neutron detection mechanism, and the relationship between measured scintillation light and energy deposited by a neutron is not accurate near and below 1 MeV. To have an enrichment measurement technique that works in the lab, we must improve our calibration of the spectrometer, so this experiment is essential. Also, we are trying to lower the neutron energy

threshold by switching from analog to digital electronics; a lower threshold may improve the measurement accuracy, but will definitely reduce the time needed to assay a 30 B cylinder in the field.

3. Several facilities have been contacted regarding field measurements for the fast neutron spectrometer. Two promising leads exist: The Paducah Gaseous Diffusion Plant hosted a Sandia visit to discuss our project needs, and Paducah has many 30 B cylinders of varying uranium enrichment and mass that would be possible to measure. Contacts with Y-12 staff have determined that it is possible to measure UF_4 (not UF_6) samples there, which would be nearly equivalent for the purposes of the spectrometry portion of this project.

Significance:

The proposed fast neutron imaging system for UF_6 cylinder enrichment measurements addresses needs of the NNSA Office of Proliferation Detection Global Nuclear Safeguards Research and Development program. This program seeks advancements in unattended approaches to cylinder weighing, identification, sealing, surveillance and enrichment measurements and full-volume assay sensitive to heterogeneous cylinders (e.g., tails) and materials substitution scenarios, which would be provided by an instrument that can independently measure and image U isotope masses inside a UF_6 cylinder. The DOE Office of Nonproliferation and International Security would also find of such technology useful.

Open Source Information Verification
151316

Year 1 of 2
Principal Investigator: K. E. Horak

Project Purpose:
The growing number of peaceful nuclear activities globally will increase the amount of nuclear material and sites that must be inventoried and tracked under safeguards by the International Atomic Energy Agency (IAEA) and analyzed by other agencies. The anticipated growth of nuclear-related activities and materials will increase the resource demand on various agencies such as the International Atomic Energy Agency (IAEA). The increased workload, along with the IAEA's responsibilities under the Additional Protocol to detect and evaluate undeclared nuclear activities, and the growing volume of information that all analysts must sort through will require nonproliferation analysts to work more efficiently and effectively. Because of the inherently geographic nature of the processes of nuclear proliferation, successful analysis requires appropriate tools for collecting and utilizing geographically referenced data to supplement more traditional safeguard activities.

Although geographic information system (GIS)-based tools are currently being developed for use in a wide variety of nuclear safeguard activities including site inspection, verification and wide-area environmental sampling, analysts tasked with gathering information to support safeguards activities generally lack the capabilities and tools necessary for extracting geographically referenced data from open sources.

This work seeks to test the hypothesis that analysts will more frequently and effectively utilize geographic information if provided with easily trainable, interoperable tools designed to systematically extract and store geospatial data from the Internet. Because of the complex nature of geospatial data, this capability will require that a diverse set of technological tools be integrated into a single package designed to integrate into the analysts' existing workflow.

Summary of Accomplishments:
There is a strong interest in open-source geospatial information and open-source tools to process it. We presented a paper at the 33rd ESARDA (European Safeguards Research & Development Association) Annual Meeting in Budapest, which was selected as best paper in its session and will appear in the peer-reviewed December ESARDA Bulletin. Additionally, we presented at the INMM (Institute of Nuclear Materials Management) 52nd Annual Meeting and at the DOE Geospatial Technology Summit (one of six papers accepted from across the Nuclear Weapons complex).

Due to the high level of interest, we have begun the process of establishing an Open-Source and Geospatial Information Working Group within INMM. An informal information-sharing group has been setup, using LinkedIn with our IAEA and ESARDA colleagues who have a common interest. A Sandia-only internal wiki has been created to contain project documents, presentations, and links to resources.

On the technical front, we have evaluated open-source research processes, developed customized versions of open-source document management and mapping software, and designed our statistical experiment for gathering user experience data.

Significance:
This research supports Objective 4.3 of DOE/NNSA's Next Generation Safeguards Initiative (NGSI), "provide information analysis solutions to improve State Level Assessments." One critical element that is currently absent from State Level Assessments is the rapid incorporation of geographic data and information to enable the IAEA to confirm State declarations in terms of declared and undeclared activities. As the IAEA moves towards making Broader Conclusions and State Level Declarations, the pressure on analysts to be both timely and accurate increases with the volume of data becoming unmanageable. This research will address these issues.

In addition to targeting IAEA Safeguards needs, this research also benefits domestic intelligence gathering and analysis. We are developing training modules for Sandia internal use that can be adapted to other US Government applications.

We anticipate integrating our work with the results from other projects such as Sensor Web. We will also investigate means of leveraging tools like CITRUS and CACTUS into the front end of our process.

Future efforts will be aimed at expanding our contribution to IAEA Safeguards, particularly in support of their 2010-2011 Research and Development mission. Tasks have already been identified in the areas of developing capabilities for exploiting geo-spatial data, collection and analysis of open-source information, search engine extension work, strategies and methods for detecting undeclared activities, and identification of new sources of information.

High-Interest Event Detection in Large-Scale, Multi-Modal Data Sets: Proof of Concept
151317

Year 1 of 1
Principal Investigator: B. R. Rohrer

Project Purpose:
The problem of processing large amounts of multi-modal data is common to the defense, intelligence, energy, and homeland security communities, and it is of particular importance when monitoring nuclear materials and watching for undeclared nuclear development activities. For many of these applications, the data processing problem involves finding rare, high-interest events. The hypothesis we propose to test is that high-interest events can be identified using anomaly detection. General, multi-modal contextual anomaly detection is a problem that has not been addressed in prior work. The purpose of the project is to find anomalies by identifying unexpected events — data observations that are not predicted either by other contemporary observations or by preceding observations.

Summary of Accomplishments:
We demonstrated the automatic creation of hierarchical feature sets in audio and visual data using the same feature creation algorithm for both. This is critical to the ability to do sophisticated prediction, as high-level features allow for more abstract representations and can make better and farther-ranging predictions than low-level features alone. Predictive ability is critical to anomaly detection, by definition. An anomaly is an unpredicted event. To a poor predictor, nearly everything will be an anomaly. To a good predictor, unpredicted events are less common and more likely to be of interest.

The technical results are described in detail in a conference publication, B. Rohrer, "Biologically Inspired Feature Creation for Multi-Sensory Perception," Second International Conference on Biologically Inspired Cognitive Architectures, Washington, DC, Nov 5-6, 2011.

Significance:
The amount of data being generated in security-critical applications is growing at an exponential rate. The military, for instance, is fielding new sensors that will increase the data volume gathered by Predators by six times. Already, a Predator mission requires 29 full-time analysts to support it. A general anomaly detection tool would multiply the effectiveness of DOE site security personnel, DOE and International Atomic Energy Agency (IAEA) nuclear material monitoring organizations, DoD information gathering forces, and Intelligence Community analysts by focusing their attention where it is likely to have the greatest impact.

Human Cargo Detection Via a Microfabricated Pulsed-Discharge Ionization Detector
151318

Year 1 of 2
Principal Investigator: R. P. Manginell

Project Purpose:
Humans are often clandestinely transported across borders to facilitate illegal immigration or malefic intentions. There is currently no automated method to detect this human cargo, or accompanying contraband or proliferation agents, during high-volume container inspection. What is required is a portable, low-power detection system that can easily be operated at checkpoints and border crossings around the world. This project will demonstrate the use of a pulsed discharge ionization detector (PDID) in detecting signatures of both human cargo and contraband compounds. In parallel with PDID instrument demonstration for this role, we will begin the engineering and development of a Microsystems and Engineering Sciences Applications (MESA)-fabricated microPDID system for portable applications.

A variety of chemicals have been identified as unique indicators of human presence. The most prevalent are propionic, isovaleric and 3-methyl-2-hexanoic acids, which are produced as byproducts of bacteria associated with the human body. Perfumes, methane, carbon dioxide, hydrogen sulfide and ammonia can also serve as less specific indicators. Field detection of relatively small amounts of these chemicals against a high background of interfering compounds represents a great technical challenge. Given these difficulties, a gas chromatograph (GC)-based sensing system coupled with a highly sensitive general detector will be required to realize an appropriate sensing system.

The most general method for laboratory analysis of such compounds involves the combination of gas chromatography and mass spectrometry (GC-MS). While miniature MS systems are under development, there continue to be difficulties with portability and the miniaturized vacuum pump systems required for operation. A microPDID system would not require such pumps, and thus would be simpler and more rugged, while still being able to detect the same range of target analytes. We propose to demonstrate the technical feasibility of such a system, initiate its design, and perform risk-reduction of the microPDID component for such a notional sensing system.

Summary of Accomplishments:
This has been a successful first year. We have procured/tested a benchscale PDID, model D-2 Valco Instruments Co. Inc. (VICI), and a half-scale D-2 prototype. This size range is important for understanding detector miniaturization scaling. The D-2 serves as a performance benchmark against which we can compare our miniaturized versions. It has also allowed us to develop well-documented methods and procedures for publications. We have designed and built a one-quarter-scale custom PDID (~10 cc total size) to further our understanding of scaling before building our microelectromechanical system (MEMS) PDID.

We have performed two types of testing: broad scoping experiments and detailed experiments on compounds relevant to long-standing applications. For the latter, we are performing limit-of-detection and other studies on dimethyl methylphosphonate (DMMP) and 3-methyl-2-hexenoic acid, which are key chemical warfare (CW) and human-contraband indicators. DMMP and ethyl-hexenoic have been tested extensively. The 3-methyl-2-hexenoic acid is presently being synthesized for us by Richman Chemical.

Scoping experiments have been performed on explosives-related compounds (trinitrotoluene (TNT), triacetone triperoxide (TATP), 2,3-dimethyl-2,3-dinitrobutane (DMNB), nitrobenzene, 2-nitrotoluene, 3-nitrotoluene), pesticides (relevant to CW, food producers, etc.), 6 key CW surrogates, trihalomethanes (water analysis), hydrocarbons, acetone, methanol and acetonitrile, (industrial applications, interferents and green-house gas (GHG) applications), air (relevant for practically all applications); and formaldehyde (a toxic industrial chemical). Thus, the PDID has demonstrated the capability to detect all chemicals of interest, given its high ionization energy.

We will begin testing our quarter-scale prototype against our D-2 benchmark. A COMSOL FEM (finite element method) model of the D2 illustrated its sensitivity to GC column position and electrode potential. A micrometer is being implemented to measure the influence of GC position. CPO (Charged Particle Optics) simulations will be used to allow a distribution of flow rates and GC positions to be modeled. Transient measurements of the plasma ignition pulse have been made to understand scaling.

We are planning at least two journal publications and a technical advance disclosure.

Significance:
We have demonstrated the extreme generality of the PDID response in Helium Ionization Detector (HID) mode. Our results indicate sub-ppb detection limits for GC-PDID. Moreover, by coupling a miniature PDID, being developed in this project, with our microGCs, we should be able to deliver ppb-level field analysis of a broad range of compounds of interest to many customers. Adding our micro preconcentrator to such a system should allow high specificity in the parts-per-trillion range. We will also be able to detect compounds previously inaccessible with sorption-based surface acoustic wave (SAW) detectors, such as fixed gases, light gases, in particular green-house gases, hexenoic acid (human contraband), and volatile signatures of pathogens and disease in livestock and humans.

We are submitting a proposal, in collaboration with UC Davis, on GC-PDID detection of volatile signatures of bacterial infections in livestock and in dairy products. In this project, we have shown that key volatile organic compound (VOC) indicators of *M. bovis* and *M. avium* infections in dairy and livestock can be detected by GC-PDID. If funded, this US Department of Agriculture (USDA) proposal will carry on this work for a much-needed application. The importance of simple methods of pathogen detection in foods is underlined by the recent outbreak of listeria in cantaloupes, which has been the worst food tragedy in the US in the past decade. This bacterial-VOC work has implications for future work in detection of human pathogens and disease.

Our work on the detection of hexenoic acid will be of interest for field detection of human contraband, hexenoic acid being a key indicator of human presence. Last summer's detection of 513 illegal immigrants in Tuxtla Gutierrez, northern Mexico, on May 17, 2011, illustrates that better methods of detecting human contraband are important.

Miniaturization of the PDID will allow better field implementation, through voltage scaling, detector volume reductions, and the future ability to mass manufacture MEMS PDIDs. Scaling of the PDID is something we are studying in this project for the purpose of miniaturization, but the ionization data provided should be useful for other fields, such as fundamental plasma physics and mass spectrometric detectors.

This project addresses many national security needs, including protecting our borders from clandestine human transport and proliferation. Ancillary benefits include producing a miniature detector that is very capable for chemical agent, explosives and greenhouse gas detection. The microPDID platform could also serve as a non-radioactive ionizer for micro mass spectrometry (or ion mobility spectrometry), or as a platform for studies of ionization on the microscale, a topic important to vacuum microelectronics. This project will be interesting to DARPA's (Microsystems Technology Office), DOE's (Proliferation Detection), and Jet Propulsion Laboratory (JPL) (Planetary Sciences and Climate Science), given the relevance to green house gas sensing.

Standoff Ultraviolet Raman Scattering Detection of Trace Levels of Explosives
151320

Year 1 of 1
Principal Investigator: T. A. Reichardt

Project Purpose:
Standoff detection of trace levels of explosive compounds has been held at the highest priority by defense and security concerns for the past decade. As a result, investments have been made toward developing optical standoff detection approaches, including visible Raman scattering, laser-induced breakdown spectroscopy (LIBS), photofragment (PF)-based approaches, coherent anti-Stokes Raman scattering (CARS), and both passive and active infrared hyperspectral imaging. Thus far, not one of these approaches has demonstrated the potential to achieve standoff detection of explosives traces on a variety of surfaces under realistic conditions. However, very recently the Swedish Defense Research Agency reported the use of ultraviolet (UV) Raman scattering for field detection of nanogram levels of explosives at 10 m, indicating that microgram levels of explosives should be detectable at distances applicable to standoff improvised explosive device (IED) detection (~130 m). Building upon these recent demonstrations, we propose to evaluate the potential of point-and-sweep, 130-m standoff detection of explosives within ~1 minute at trace levels by UV Raman scattering on typical surfaces, for use either as a stand-alone approach or as a confirmatory channel.

The UV-Raman-scattering detection limit will be assessed from the signal strength compared to backgrounds and interferences (all measured in the laboratory) as well as potential noise sources (characterized from fluorescence-light-detection-and-ranging [LIDAR] field data). Compared to the aforementioned alternatives, we note four differentiating features of UV Raman scattering: 1) Raman scattering is non-destructive, allowing repeatable optical sampling and signal averaging, 2) Raman scattering potentially allows the use of eye-safe laser fluences at UV wavelengths, 3) the use of UV lasers corresponds to Raman shifts of ~10 nm, less than the Stokes fluorescence shift from common materials, providing "background-free" measurements, and 4) Raman scattering provides a unique chemical fingerprint of the molecule for improved specificity.

Summary of Accomplishments:
A calibrated continuous-wave (CW) UV (244-nm probe) mini-Raman-LIDAR instrument was assembled and characterized. Quantitative amounts of trinitrotoluene (TNT) were deposited on a gold-coated surface and probed with the instrument. We demonstrated Raman scattering signal levels from TNT consistent with the literature reports. We note, however, that the signal level does not scale linearly with concentration. Rather, due to the absorption by TNT, with a literature-reported 244-nm absorption cross section of 6×10^{-17} cm^{-2}, the laser penetrates only ~50 nm into the sample, so any deposit of higher concentration is subject to optical thickness effects. For such deposits, rather than a Raman scattering cross section with units of cm^2/sr, it is better to consider a Raman scattering albedo, with units of J/mJ-sr.

Our measured Raman scattering albedo was incorporated into a performance model that focused on standoff detection of trace levels of explosives. The Raman scattering detection of explosives depends on both the signal strength and the distinguishability of the explosive signature from that of other materials. In an effort to assess the distinguishability of the TNT Raman spectrum from common backgrounds, UV Raman spectra were also acquired for a number of anticipated background surfaces: tile, concrete, aluminum, cloth, and two different car paints (black and silver). While these spectra contained features in the same spectral range as those for TNT, we did not observe any spectra similar to the spectrum of TNT.

Significance:

Standoff explosives detection is held at the highest priority by the DHS, the Defense Threat Reduction Agency (DTRA), and the Joint Improvised Explosive Device Defeat Organization (JIEDDO). Performing a systematic study of the sensitivity and specificity of UV Raman scattering from quantifiable amounts of explosives deposited on typical backgrounds will provide the knowledge necessary to evaluate the utility of the approach for detection scenarios of relevance to these customers.

Predictive Modeling of Non-Ideal Explosives
151321

Year 1 of 3
Principal Investigator: R. G. Schmitt

Project Purpose:
Homemade explosives (HMEs) and improvised explosive devices (IEDs) are an increasing domestic threat and are commonly used in foreign conflicts dominated by sectarian disputes and/or non-state terrorists. Protection or countermeasures against these weapons could be significantly improved with a better technical understanding of their behavior. Termed "nonideal" explosives (NXs) because their behaviors are not well represented by classical detonation theory and scaling laws, relatively little fundamental research has been conducted to characterize their performance, and predictive numerical modeling is largely absent. An improved level of understanding will rely on the tightly coupled pursuit of experiment, theory, and numerical modeling. Numerical modeling is essential for the discovery of reaction mechanisms and for simulating the coupled, nonlinear evolution of composition, temperature, and pressure of the reactive flow behind a shock front in highly heterogeneous media. Novel and systematic experimental research is required to characterize important phenomena relating to the high-pressure equation of state and shock behavior. Experimental and numerical research is required to advance the theoretical understanding upon which an appropriate numerical model and methods to solve the model are constructed.

The research challenge in understanding and modeling NXs is one of determining the fundamental atomistic and mesoscale mechanisms underlying the controlling phenomena and then bridging the multiple length and time scales to accurately represent the effects of these phenomena in numerical simulation codes. Because these studies have not been done for NXs, the challenges they present remain cutting-edge research. Success in this endeavor lays the necessary groundwork for developing the numerical methods needed for predictive modeling of NX scale effects. The proposed work is a step toward having the tools needed to answer specific questions about the effects of NXs.

Summary of Accomplishments:
We successfully implemented a chemical equilibrium code into CTH (a multi-material, large deformation, strong shock wave, solid mechanics code) as a primary equation of state. The methodology has been tested on simplified problems and areas for improvement have been identified. A simplified extension to the history variable reactive burn model was incorporated into CTH and compared to a variety of ammonium nitrate and fuel oil (ANFO) experiments. Initial results suggest that the proposed model we are developing under this project will be able to predict ANFO reactive flow properties. A framework for the proposed multistate modeling formalism was incorporated into CTH. The framework allows for the extended states required to model the complex chemistry and hydrodynamics of ANFO. The framework includes two new formalisms for performing reactive flow simulations within CTH. The simplified formalism mimics existing literature technology while the new advanced formalism borrows concepts from continuum mixture theory. We have developed a viscous relaxation model for the interparticle porosity present in a variety of nonideal explosives. This model has been implemented into CTH and is undergoing evaluation. In addition, methods for evolving the intraparticle porosity are under active development. During the past year, we have performed a series of gas gun experiments at several impact velocities into samples of ANFO. In addition, a variety of CTH simulations from continuum scale down to mesoscale have been performed and are being analyzed. These simulations compare favorably with the experiments and are providing new insight into the important hydrodynamic processes for ANFO. We have capitalized upon the development of a molecular dynamics potential for

ammonium nitrate at Penn State University. This potential has been explored with respect to the phase behavior of ammonium nitrate (AN) crystals, and studies are beginning to analyze AN in shock flow.

Significance:

Current computing capabilities and new ideas and approaches for modeling NXs, given growing concerns about these materials, make it timely to improve the modeling and apply modern simulation methods to investigate and characterize their reactive flow. The desired technical advances would enable simulation tools that could benefit DOE, DHS, and DoD by enhancing threat assessments and substantially accelerating development of economical counter measures against HME and IED weapons. This project expands understanding needed to create a predictive simulation capability for NXs.

Desorption Electrospray Ionization – Differential Mobility Spectrometry (DESI-DMS) for Homemade Explosives Detection
151322

Year 1 of 2
Principal Investigator: C. L. Rhykerd, Jr.

Project Purpose:
An investigation of a new trace detection method is proposed. There is potential to detect a much larger analyte list (hundreds vs. about ten) using conventional trace methods (such as ion mobility spectrometry) by integrating a desorption electrospray ionization (DESI) source with a differential mobility spectrometer (DMS). Investigations will focus on homemade explosive chemicals (explosives, oxidizers, fuels, and precursor chemicals). DESI-DMS has not been studied previously.

General questions about the DESI-DMS technique:
- What phenomena are observed for the homemade explosive analytes?
- What ions are observed, in what polarity, and at what temperatures?
- Does it detect a wide enough range of analytes to be useful in field applications?

- Fundamental scientific questions about the ionization and detection processes:
- What is the efficiency of ionization as a function of swab material (cotton, steel mesh), angle of incidence, distance from the sample, and spray liquid (water, methanol)?
- What is the ion lifetime (longer lifetimes enable additional specificity)?
- What is the maximum resolution achievable (to reduce nuisance alarms and resolve similar molecules)?

Previous work has focused on either lab-only techniques (mass spectrometry) or a very short list of common high explosives. This work will anticipate the terrorists' explosive choices by developing a method that is suitable for a wide range of explosive materials and is fieldable for screening applications.

Sandia will be the first to discover the capabilities of the DESI-DMS method. There is always risk in discovery, and it is impossible to predict what ion chemistries we will observe. However, based on the previous work, we expect to succeed with the proposed approach. The proposed project is the up-front science and engineering that will enable such a future application for DHS, DoD, or DOE.

Summary of Accomplishments:
We built a DESI-DMS. The DESI unit was purchased from Prosolia; the DMS was acquired from New Mexico State University. We demonstrated the ability to detect ions formed with the DESI with the DMS. We investigated the use of paper spray ionization with DMS detection for several chemicals.

Significance:
The project is focused on discovering science and engineering to enable field detection of a wide variety of homemade explosives. National security application include: 1) domestic transportation security screening including airports for DHS, S&T, and the Transportation Security Administration, 2) suicide bomb / vehicle bomb screening overseas for DoD/Joint Improvised Explosive Device Defeat Organization, and 3) Special Agent Bomb Technician response for the Federal Bureau of Investigation. The primary significance of the work is investigation of a potential method to form ions from explosive materials of interest for analysis by a fieldable method.

Advanced High Security Command and Control Interface (AHSC2I)
151323

Year 1 of 3
Principal Investigator: D. E. Small

Project Purpose:
The current generation of alarm, communication and display (AC&D) systems used in high security facilities across the DoD and DOE/NNSA enterprise have significant functional deficiencies which hinder operators from maintaining situational awareness in emergency situations, which is especially true when bad weather causes high nuisance alarm rates (NAR). We will characterize existing system operator functions in high NAR /emergency situations, working with end-users to identify specific deficiencies and creating unique technological solutions to address those deficiencies: the Advanced High Security Command and Control Interface (AHSC2I).

The AHSC2I will support all aspects of battle space management and control that will:
- Enable multiple operators to deal with adversaries in parallel using a digital map/multi-touch concept.
- Employ a geo-referenced, realistic 3D site model of terrain, buildings and all sensor and video data.
- Implement an advanced training mode, compatible with constructive simulations (Joint Conflict and Tactical Simulation [JCATS], simulation software for NNSA [Dante], and others).
- Monitor physical-security-system state of health to cue operators when performance is degraded.
- Support an open standards-based interface, allowing for quick integration.
- Enable geo-referenced data fusion from advanced concept sensors using real-time visual tracking of adversaries using automated pan, tilt and zoom (PTZ) camera networks to localize potential targets.
- Enhance alarm analysis in NAR/FAR (false alarm rate) conditions to include real-time weather data.
- Implement rules-based filtering of alarm events enabling automated assessment prioritization. Provide definable, automated quick reaction checklist for critical guidance and cue system operators to critical actions required during emergencies.

To validate the AHSC2I, we will build two training prototypes:
- A standard AC&D system, representing currently deployed hardware.
- An implementation of the AHSC2I concept.

Constructive simulation will be used to provide realistic training scenarios to both systems. Studies will compare the performance of operators on both systems against virtual/constructive simulations to determine efficacy.

Summary of Accomplishments:
Sandia personnel traveled to a representative high-security site in April 2011 in support of the AHSC2I LDRD project. The purpose of the trip was to observe real-world use of a deployed perimeter security system and collect context of use information as described above to assist the team in identifying areas that would benefit from system improvements. As part of the trip, the team interviewed 15 personnel in various positions. A detailed task analysis report of most key positions in and around AC&D operations was performed. This report helped to guide design decisions that are currently being made with regard to the user interface and communications framework.
We have developed a network-based framework for testing and evaluating a variety of user interface implementations that will allow for interaction with and designation of specific alarm areas on a 3D virtual terrain model of a high-security site. The framework utilizes advanced networking infrastructure that allows for low-latency high-speed alarm reporting and response. Developed components include: 1) simulator for sensor responses and communicating those as alarm events, 2) an alarm server that

distributes alarm signals to client applications, 3) an alarm database for logging alarm signals, and associated user actions, 4) video server capable of receiving and redistributing live and recorded video, 5) video sources include actual cameras and simulated cameras in a virtual environment, 6) a 3D user interface for interacting with alarm events written in native C++ code, and 7) a 2D user interface that uses HTML5 and web services.

We have also developed modeling and simulation capabilities to provide new sensor models for the Umbra Simulation framework. These sensor models are being developed to realistically represent the performance of actual deployed sensors at current facilities and include the full suite of sensors used in high-security facilities.

Significance:

We completed a significant knowledge elicitation of the job functions and task description in and around the AC&D systems in a high-security environment. This report stands alone and will be of use to user interface researchers in the future. Development of the overall user interface / networking framework will enable user interface studies that are planned for FY 2012. We have analyzed the job of the AC&D operator sufficiently to create a new interface that addresses shortcomings that are unique to high-security sites.

This research is developing modeling and simulation capabilities to provide new sensor models for the Umbra Simulation framework. These sensor models are being developed to realistically represent the performance of actual deployed sensors at current facilities, including but not limited to buried cable sensors, vertical taught-wire sensors, security camera models, and passive infrared and bi-static microwave sensors. The models are based on first principles physics such that the sensor's detection or failure is based on parameterized fundamental sensor physics. This enables adjusting the energy transmission and detection to validate the performance from a variety of targets. The simulation environment enables creating realistic and accurate site models with high fidelity 3D terrains and contains a scenario editor to script attacks on the facility. It can select appropriate behaviors to represent the attacker's operation. The execution of this simulation environment will be connected to a real-time AC&D operator interface providing simulated views from cameras and simulated sensor events. This will provide us with the capability to perform evaluation of specific user interface improvement by creating representative, reproducible stimuli for user interface studies that are scheduled in FY 2012. It will also allow for the creation of a virtual training environment that will enable evaluating and identifying any system deficiencies that could hinder operators from maintaining situation awareness.

This research will advance our understanding of how humans interpret data in time-critical, high-consequence situations. By doing this, Sandia will advance national security by providing security commanders in critical facilities better tools for detecting, assessing, and responding to attacks. The current tabletop communication model will be digitally enhanced to allow multiple operators to participate in rapid-fire decision-making, communication, and control to maintain superior situational awareness. AHSC2I will increase the speed at which operators can confirm or rule out hostile acts from Wide Area Detection Systems, perimeter intrusion detection and assessment systems, and interior alarms.

Genomics-Enabled Sensor Platform for Rapid Detection of Viruses Related to Disease Outbreak
151324

Year 1 of 3
Principal Investigator: S. M. Brozik

Project Purpose:
Bioweapons and emerging infectious diseases pose growing threats to our national security. Both natural disease outbreaks and outbreaks due to a bioterrorist attack are a challenge to detect, taking days after the outbreak to identify since most outbreaks are only recognized through reportable diseases by health departments and reports of unusual diseases by clinicians. The development of more rapid diagnostic assays for virus detection with high sensitivity and specificity will be very useful for the management and treatment of patients, for epidemiological surveillance, and for deployment in sensor systems for use in transportation hubs, at borders, or for threat detection by the military. Viruses can be isolated from the blood of someone infected early on when immunoglobulin antibodies may not be detectable. However, typical methods for detection involve virus isolation through tissue culture assay with long incubation periods of a week. Molecular diagnostic systems for ribonucleic acid (RNA) detection are much faster but still require time-consuming steps and are not yet portable. We propose ultrasensitive, direct, hybridization-based RNA detection systems, requiring small sample sizes and short detection times for field and clinical use. Though detection of RNA is difficult because of its lack of stability and extraction from the virus, the pay-off of a high throughput screening capability during emergency response or outbreaks is enormous for public health and military safety. Two independent assays will be developed to address the many challenges of RNA detection. We will also take advantage of the recent explosion of genomics data on many arboviruses, including several of those widely considered most important to public health and national security, providing a novel opportunity to leverage this data for diagnostic benefit as well as biothreat detection.

Summary of Accomplishments:
We have assessed suitable primers for West Nile Virus RNA detection. Eight primer sequences from three different coding regions (E, NS3, and NS5) have been selected and synthesized with the appropriate end group modifications for binding to both glass and indium tin oxide (ITO) substrates. The baseline experiments for single DNA/RNA optical detection are complete. We have optimized the experimental details for the surface immobilization of reverse transcriptase (RT) to pristine optical substrates. We have completely characterized the bioassemblies. We have: 1) measured the surface density of available biotins, 2) measured the surface density of streptavidin (SA) specifically bound to the available biotins, 3) determined that the ratio of SA to RT is 1:1, and 4) virtually eliminated all non-specific interactions between the surface and, DNA/RNA, RT, and SA. We have also verified the activity of the surface attached RT through the use of a polymerization assay and have finished the synthesis of the primer labeled quantum dots (p-QD) that will be used in the detection scheme. Finally, we have determined the dissociation rates of DNA/p-QDs from the surface immobilized RT. We have started to design the microchannel for the optical sensing system including fabrication process, packaging method post conjugation, integration, and alignment/calibration method.

For the electrochemical assay, we have optimized a detection protocol where we immobilize the guanine substituted DNA probe to the surface via a phosphonoundecanoic acid linker and detect the RNA sequence containing guanine through a ruthenium bipyridine catalyst. We have tested the detection assay on bulk ITO and are in the process of optimizing the assay within a 21-channel microfluidic array. We are also characterizing surface density of DNA probes on the array and are developing a phosphonoundecanoic acid-PEG (polyethylene glycol) molecule to passivate the microchannel walls and adhesive.

Significance:
The project has potential benefit to both applied and basic science interests at Sandia. This project positions Sandia to respond to specific needs of homeland security agencies. The sensor systems will be part of the capabilities this investment area is developing to counter weapons of mass destruction. We plan to develop two sensor system prototypes that can eventually be deployed as biological detection systems for use in transportation hubs, at borders, and in public health labs for clinical diagnostics. The project is advancing core expertise in biological sensing and engineering solutions for integrated fluidic systems.

Homeland Security, Defense Advanced Research Projects Agency (DARPA), and Defense Threat Reduction Agency (DTRA) could each benefit from an ultrasensitive high-throughput sensor system that could detect either RNA or DNA. Specifically, these sensor systems could be used by the military for use in the field to detect biothreat agents in situ. Biodefense and trade agencies usage includes testing for biothreat agents during quarantine and at borders. In addition, hospitals would benefit from their use at the point of care during outbreak or emergency situations. Finally, public health surveillance and diagnostic labs could perform rapid simple detection analysis to monitor arthropod, animal and human specimens during routine sampling.

High Energy Resonance Radiography by Double Scatter Spectroscopy
151325

Year 1 of 3
Principal Investigator: P. Marleau

Project Purpose:
Efficient inspection of airline baggage and cargo containers at airports, seaports, and border crossings is critical to homeland security. The majority of inspection systems installed today uses x-rays or gamma rays, which are primarily sensitive to the density of interrogated materials. Techniques using multiple-energy x-rays and/or fast neutrons can achieve limited material composition identification; however, these techniques have a serious drawback in that they require expensive and complicated radiation sources. This project seeks to develop a new technique for the non-intrusive detection of explosives, illicit drugs, and radiological/nuclear threats using a combination of fast neutron resonance and gamma-ray imaging with readily available commercial radiation sources. The proposed technique will allow for high-energy neutron and gamma-ray interrogation over a large range of energies and viewing angles. As a result, material composition identification by resonance imaging and 3D tomography without rotation of the target can be achieved. The system that we propose will be capable of material identification and 3D imaging using fast neutrons and/or gamma rays. This would typically require the use of a complex and expensive radiation source. We propose that by placing a segmented plane of gamma/neutron detectors between a mono-energetic source and the target, we can interrogate with a range of energies at multiple angles. Determination of mass density is made possible by differences in the absorption of neutrons and gamma rays. Most elements have resonant features in their neutron absorption spectra allowing for further material composition identification.

To our knowledge this novel technique has never been attempted. There will be many technological issues to overcome including achieving high interaction rates and providing adequate time resolution and neutron/gamma discrimination. The primary risk of this technique will be achieving sufficient efficiency at a reasonable cost/system complexity; however, the fidelity of the measurement should improve the signal to noise, significantly mitigating this risk.

Summary of Accomplishments:
To support experiments to validate Monte Carlo models and prove the concept with actual measurements, we established a new fast neutron radiography laboratory. The laboratory consists of a shielded high bay cell where D-T and D-D neutron generators can be run and a control room where MOWs can safely and remotely run experiments.

The initial test system that we constructed for these experiments consists of 2 – 2” diameter x 2” deep aluminum cells filled with EJ-309 liquid organic scintillator coupled to 2” photomultiplier tubes (PMTs). A newly procured Thermo MP320 Deuterium-Tritium neutron source is rotated about an axis centered on the “near” scintillator cell. A Mesytech MPD4 unit provides pulse shape discrimination (PSD) on the PMT pulses and allows us to separate neutrons from gammas. Data is collected in list mode for post processing.

This system has been tested with an assortment of target materials: H_2O, ammonium nitrate, high-density polyethelyne, and graphite. Initial results are extremely promising. The transmitted energy distribution with no target is compared to that with target to measure the attenuation as a function of energy. The difference between the un-attenuated empty data set and the target data set is used in a chisquared minimization to determine the elemental densities. The best-fit values were within 10% of calculated values for all materials.

Feasibility has been established and initial models of full-scale systems indicate that this will be a viable technique.

Significance:
Despite its benefits, fast neutron radiography has not been a practical alternative to x-rays as a primary screening method. This has primarily been due to the impracticality and cost of adequate radiation sources for existing techniques. If successful, the technical advances represented in this proposal will significantly improve the ability to locate and identify explosive and nuclear threats. DHS S&T, Federal Aviation Administration (FAA), and International Atomic Energy Agency (IAEA) are a just few of the agencies that have interest in an advanced screening technology of this type. If successful, we expect that DHS S&T or Domestic Nuclear Detection Office (DNDO) would support the further development of this technology toward commercialization.

Enhanced Micellar Catalysis
151326

Year 1 of 2
Principal Investigator: R. Betty

Project Purpose:
Sandia's DF-200 decontamination formulations are a proven, rapidly effective solution for decontamination of chemical/biological warfare (CBW) agents. However, little is known or understood about the fundamental parameters of micellar catalysis that enable this successful CBW decontamination chemistry.

We propose to integrate two highly successful technologies — high-quality thin films and DF-200 CBW decontamination formulations for the development of an enhanced understanding of the DF-200 micellar catalysis decontamination mechanism. By leveraging on the surfactant micelle-based backbone common to both of these domains, we propose to initially focus on an investigation of micelle and vesicle properties and strategies to enhance the micellar catalysis decontamination mechanism achieved through these surfactant systems. Various current deployment methods will benefit from the incorporation of enhanced micellar catalysis knowledge, demonstrated by increased efficiencies in capacity and neutralization. The technical challenges to determining this information are not excessive, and Sandia has the expertise and instrumentation to accomplish the technical tasks.

Success of the DF-200 technology has been achieved without the benefit of building from known fundamental key physical and chemical properties and conditions at the micellar and molecular level that impact performance. Therefore, it is very likely that performance optimization has not yet been achieved.

Summary of Accomplishments:
In the first year, we began to collect preliminary data establishing baseline DF-200 micellar catalysis parameters with the goal of determine micellar characteristics of standard, modified efficacious, and "poor performing" formulations. Dynamic and static light scattering techniques were employed to analyze the size of the micelles formed in solutions. Consistent information on micelle size could not be acquired using light scattering methods, despite the attempted use of three different instruments. Through recommendation of a fellow Sandian, University of Minnesota (UMN) Characterization Facility personnel were contacted to perform scoping small-angle x-ray scattering (SAXS) and cryo-TEM (transmission electron microscopy) analyses. Preliminary SAXS data evaluating the micelle size distribution and shape of dilute Variquat 80MC (the primary quaternary ammonium surfactant in the DF200 formulation) indicated spherical micelles over a broad size range, averaging around 9 nm. The preliminary cryo-TEM data suggested spherical micelles ranging from 15-25 nm. Further SAXS analyses may require alternate modeling approaches within the SAXS software or evaluation of less viscous solutions. A contract was placed in May 2011 for UMN to perform additional SAXS and cryo-TEM analyses to determine micellar conditions of various surfactant blends.

A new aerosol test chamber was designed and fabricated with the objective to characterize droplet size, distribution, chemistry, and compositional change between aerosol and gas phases over time. Charged and uncharged droplets produced from the ITW rotary atomization nozzle will be evaluated; system parameters such as applied voltage, liquid flow rate, shaping air flow rate, rotary cup velocity will be varied. Test parameters and conditions (temperatures, flows, and humidity) will be continuously monitored and logged. The particle size and distributions will be measured by use of the Aerodynamic

Particle Sizer (APS) and Scanning Mobility Particle Sizer (SMPS). Gas Chromatography with a Mass Spectrometry detector (GC/MS) will be used to measure chemical (organic) compositions of the aerosol and vapor phases.

In FY 2011, preliminary surfactant micellar particle shape and size data characterizing the surfactant component of EasyDecon (Sandia's patented and commercialized formulation for CBW agent decontamination) was provided by UMN Characterization Facility. SAXS and cryo-TEM techniques characterized the micelles as spherical in shape, having an average micellar size of 9 nm, with a distribution from 15 - 25 nm. Follow-on testing of micellar environments in alternative cationic surfactants was inconclusive. Because UMN expertise in this area is no longer available, additional SAXS and cryo-TEM expertise will be sought at another facility.

We established a test approach to evaluate the micellar environment and decon chemistry of aerosolized decontaminant sprays. Initial tests to characterize the rotary atomized spray droplet distribution using baseline nozzle and system conditions were conducted. Under baseline conditions, a bimodal distribution was observed with the predominant mean droplet size distribution between 1-2 microns and with a smaller droplet size distribution of approximately 700 nm. There was evidence that the larger portion of the distribution was shrinking in concentration over time, most likely due to evaporative losses. The characterization of aerosolized decontaminant droplet chemistry (FY 2012) both in aerosolized particles and in the vapor phase will increase our understanding of reactive species and effective concentrations in these environments. Once aerosolized droplet chemistry is understood, rotary atomization spray nozzle and system parameters will be varied, and/or formulation modification will be made to increase the effectiveness of aerosolized decontaminant sprays.

Significance:
It is anticipated that the micellar characterization of effective and ineffective formulations will inform future development of application-specific decontaminants. Results may suggest formulation and/or deployment method modifications, optimizing the efficacy of micellar catalysis across broad use for neutralization of liquid, aerosolized particle, or vaporous phases of contamination. Incorporation of enhanced micellar catalysis knowledge into current decontamination deployment methods will expand Sandia’s expertise and capabilities in CBW decontamination technology.

The commercial and government needs are broad and, for many applications, already very well established. Potential applications exist for DHS, military agencies (Defense Threat Reduction Agency [DTRA]), and US Army Non-Stockpile Chemical Materials Agency (NSCMA), and public health and transportation industries.

Anomaly Metrics to Differentiate Threat Sources from Benign Sources in Primary Vehicle Screening
151327

Year 1 of 1
Principal Investigator: W. Mengesha

Project Purpose:
Radiation portal monitors (RPMs) are deployed at ports of entry (POEs) to screen vehicles and containers for the presence of radiological threats. Since the poly-vinyl toluene (PVT) gamma-ray detectors used in RPMs lack the energy resolution for unambiguous isotopic identification, alarm metrics are based on gross counts and/or energy window ratios from different detectors (e.g., gamma ray or neutron). Because naturally occurring radioactive materials (NORM) are ubiquitous in commerce, the sensitivity of RPM detectors to threat sources depends on their ability to differentiate between benign and threat sources. Existing alarm algorithms lack the ability to differentiate benign and threat sources with high confidence, as their thresholds are based on detecting set quantities of specific materials. Current S&T has addressed this problem through improvements in detector technologies. We propose to address it through the better use of data collected by these detectors. Anomaly detection metrics can be used to differentiate signals as benign or anomalous by comparing single measurements with historical measurements of benign sources. Anomalies are signals from sources other than NORM and include threat, medical, and industrial sources. We propose to apply data mining and sensor fusion methods to the analysis of RPM data. A Bayesian statistical decision approach will be used to calculate the probability of a source belonging to the benign source population for a given level of specificity. Key challenges include developing a model of the benign source population from multisensor data and selection of appropriate anomaly thresholds.

We propose to study the feasibility of adapting generalized techniques from statistics to the analysis of RPM data. The proposal has high potential impact as the capabilities developed in this work could be used in deployed and future systems to improve NORM discrimination and/or improve the sensitivity to weaker threat sources. The risk in this project is primarily related to potential difficulties in adapting these techniques to this type of data.

Summary of Accomplishments:
Anomaly detection techniques implemented in the present study, namely Principal Component Analysis (PCA) and Cluster Analysis, showed improvements in sensitivity and specificity of discriminating benign source population from threat source population as compared to the traditional gross counts approach. Encouraging results have been found in the performance of the techniques. Clear improvements have been found in the false alarm rate (FAR) compared to the traditional gross counts threshold approach. The PCA technique coupled with clustering can be beneficial in defining optimal and minimized thresholds for alarming at POEs. This, however, was not observed in the present study. This will be investigated in detail in future work. The present work was not able to investigate optimization of energy windows used in the analysis. Further enhancement in anomaly detection is sought using iterative maximization of feature variances in principal components (PC) space by varying energy windows. Data used in the analysis represent static and simulated data. It is not characterized by temporal features and other uncertainties related to actual measured data. These may include gain variation in the RPM detectors, electronic noise, and other systematic errors that can cause significant deviation from Poisson statistics. Implementation of investigated techniques using measured data is required to address these issues.

Data fusion was not implemented for enhancement of sensitivity using neutron and gamma information. Current investigation has determined that fusion of neutron and gamma data will not have an impact on sensitivity enhancement, as the neutron data alone will enable the discrimination of benign sources from threat sources using the gross counts approach.

Significance:
It is known that benign sources can trigger radiation alarms at POEs that require additional inspection and resources to assure security. Benign-source-caused alarms are commonly known as “nuisance” alarms and can have a significant impact on traffic flow, economy, and operations at POEs. Plastic scintillators and helium gas detectors are the most widely used RPM detectors for gamma and neutron emission detection, respectively, and are used for screening cargo and vehicles at POEs and land crossings. Plastic scintillators are the cheapest gamma detectors that can be found in the market, which explains the reason for their wide deployment. However, due to their inherent poor energy resolution, they lack the capacity for discriminating threat sources from benign sources based on resolved photo peaks. However, their disadvantages in discriminating benign and threat-source energies can be reduced by implementing advanced post data acquisition analysis. Anomaly detection using advanced statistical techniques has been shown to enhance the sensitivity and specificity of RPMs at POEs. This will inevitably result in better performance with significantly reduced alarm rates. The reduction of the alarm rate will have a significant impact in the economy by allowing smooth flow in traffic and commerce and by significantly reducing the requirements for additional resources to carry out a secondary inspection. Further, the present study has the potential to support a variety of DHS and DOE national security missions. The use of anomaly detection in deployed RPM systems at Customs and Border Protection (CBP) ports of entry has the potential to improve operational effectiveness by improving NORM discrimination in primary inspections, thus decreasing the secondary inspection workload. Furthermore, the techniques are of significant interest to Domestic Nuclear Detection Office (DNDO) and Defense Threat Reduction Agency (DTRA).

Simulation-Based Strategic Analysis of Complex Security Scenarios
154570

Year 1 of 2
Principal Investigator: Y. Vorobeychik

Project Purpose:
Many advanced technical tools are available to protect computing resources that, in principle, enable a high level of sensitive information protection. Nevertheless, cyber attacks remain exceedingly common and successful. While traditional analyses of security problems have succeeded in producing good technical solutions, they have often ignored the human factor integral to these problems. Human attackers expend substantial effort to crack secured systems because they have the incentive for doing so. People involved in implementing security follow individual incentives, which need not align with global security concerns; consequently, desired security solutions are often implemented poorly or not at all. This complex interplay between individual incentives and global (organizational and/or national) goals can be modeled and analyzed using game theoretic techniques. By analyzing not only what is possible but also what is motivated, a holistic approach to the cyber security problem can be developed, informing policy and providing tools to policy makers. The goal of the project is to construct realistic game theoretic models that unify several current incentive-based approaches to security and to develop simulation-based methods for analyzing such models that exploit the high-performance computing capabilities at Sandia. Specifically, we will develop a model with many interacting players responsible for security decisions and many possible attackers whose preferences are uncertain to the defenders. Such a general model formulation has yet to be addressed, and it requires a radically different computational approach from the existing formulations. For the first time, this work will marry large-scale simulations of realistic systems to game theoretic analysis. We will focus on the behavior of game theoretic solutions with system scale, structure of interactions between players, and response to policy instruments (e.g., subsidies, penalties, etc.).

Summary of Accomplishments:
In FY 2011, the project team successfully created a general model of single attacker/defender interaction in highly interdependent settings. Traditionally, security decisions have been made without explicitly accounting for adaptive, intelligent attackers. Recent game theoretic security models have explicitly included attacker response in computing randomized security policies. Such models have already enjoyed considerable success and adoption, with high profile examples including ARMOR (a system deployed at LAX since August 2007) in the context of airport security and intelligent randomization in scheduling (IRIS) federal air marshals. Techniques to date, however, generally fail to explicitly account for interdependence between the targets to be secured, which is of vital importance in a variety of domains, such as critical infrastructure security. We introduced a novel framework for computing optimal randomized security policies in networked domains that extends previous approaches in two ways. First, we extend previous linear programming techniques for Stackelberg security games to incorporate benefits and costs of arbitrary security configurations on individual assets. Second, we offer a principled model of failure cascades that allows us to capture both the direct and indirect value of assets. Finally, we use our framework to analyze four models: two based on random graph generation models, a simple model of interdependence between critical infrastructure and key resource sectors, and a model of the Fedwire interbank payment network. Additionally, the team created a novel framework and algorithms for solving adversarial patrolling settings, considerably advancing the state of the art in both speed and solution quality. Finally, we analyzed quality of strategies in simple, abstract multi-player security settings, with implications for public policy, such as subsidies for security investment decisions.

Significance:

This project has direct relevance to cyber security and security domains more generally, insofar as we propose an entirely novel set of modeling and analysis techniques to address the problem of security by combining the enabling technical capabilities with human decision-making. Both human decisions and technical tools are of vital importance to national and organizational security policy.

Refereed Communications:

Y. Vorobeychik, J.R. Mayo, R.C. Armstrong, and J.R. Ruthruff, “Noncooperatively Optimized Tolerance: Decentralized Strategic Optimization in Complex Systems,” *Physical Review Letters*, vol. 107, p. 108702, September 2011.

Multi-Objective Optimization Approach for Multimodal Information Retrieval
154694

Year 1 of 2
Principal Investigator: B. S. Paskaleva

Project Purpose:
A principal goal of multimodal information retrieval (MMIR) is extraction of relevant information from large heterogeneous databases. To this end, user's information needs are abstracted into sets of formal queries and the database is ranked by similarity functions, which compare the queries against a database.

A key open problem in MMIR is the development of similarity functions that maximize the relevance of the ranking with respect to the user's information needs while minimizing the probability of error. Because different similarity functions expose different aspects of the match between the database and the queries, we propose to rank the database using a superposition of similarity functions, optimized with respect to utility measures expressing relevance.

To address MMIR challenges, we propose a two-stage approach that draws upon ideas from optimization, control, and approximation theory. The first stage aims to establish a formal methodology for maximization of ranking relevance by formulating the task of finding optimal superposition of similarity functions as a reference multi-objective constrained optimization in Banach spaces. The second stage focuses on the approximation of the reference problem by finite-dimensional convex optimization problems or linear programs, which can be solved efficiently.

Lifting of MMIR into an abstract setting separates our approach from existing methodologies, which are often dominated by ad-hoc or problem-specific algebraic techniques. In so doing, we aim to discover basic design principles that can be adapted to solve diverse MMIR problems: detection of nuclear weapons proliferation, rapid determination of anomalies and bio-threats, effective early detection of physical and cyber attack against energy grids, arising in strategic NNSA and DOE themes. Therefore, if successful, this effort will support the core mission of Sandia and its future growth in these areas. Our previous experience and collaborations with leading researchers in classification, pattern recognition and optimization gives us confidence that we will be able to succeed in the project.

Summary of Accomplishments:
We focused on four key tasks which establish foundations for the future work: 1) formulation of a Generalized Vector Space Model (GVSM) for MMIR, 2) formulation of an abstract definition of entity resolution problem, 3) identification of representative, publicly available databases for testing of the framework, and 4) development of matrix laboratory (MATLAB) code for testing of the optimization approach for the selection of superposition of similarity measures.

Development of the GVSM is one of the key accomplishments of the project. GVSM defines a mathematically formal framework for consistent representation of a wide range of MMRI problems. It allowed us to formulate: 1) an abstract definition of the entity resolution problem and 2) to obtain consistent extensions of set-based similarity measures to documents comprised of token multisets and using norms beyond the L1 norm, which is another key accomplishment for the project.

To focus the development of MATLAB MMIR capability, we selected benchmark datasets for entity resolution developed by the computer science department at the University of Leipzig, such as the product entities from the online retailers, Abt- Buy.com. A major goal of this project is to develop an optimization approach for the selection of an optimal superposition of similarity measures, which maximizes the relevance of the ranking with respect to the user needs. Our initial approach formulated and implemented constrained optimization for an optimal superposition of the generalized similarity measures provided by the GVSM framework, in the context of the entity resolution problem. The objective function is defined using the training set from the Abt-Buy.com database. The performance of the resulting synthetic similarity measure was evaluated using testing sets from the same database. We studied the sensitivity of the approach with respect to the size of the training set, different norms, and constraints used in the optimization.

Significance:

Homeland, energy, and infrastructure securities lead to challenging MMIR problems arising in multiple contexts such as detection of nuclear weapons proliferation, rapid determination of anomalies and bio-threats, and effective early detection of physical and cyber attack against energy grids. Accurate and efficient solutions are required to support the missions of DOE and NNSA, yet remain the bottleneck for utilizing huge amounts of diverse data in the decision-making process.

This project aims to develop mathematical formalism for MMIR problems that allows one to discover their common mathematical structures. In so doing, we will enable the development of a flexible MMIR approach applicable to the range of problems described above. The generalization of the vector space model (VSM) for information retrieval, developed in FY 2011, defines a consistent vector-space representation of a wide range of MMIR problems. Our work formalizes mathematically the key building elements of the VSM and defines weighted document norms. The weighted document norms allowed us to extend norms of set-based operations between documents, such as union and intersection, defined only when the documents are sets of tokens, to documents comprised of multisets of tokens. This, in turn, allowed us to obtain consistent extensions of set-based similarity measures such as Jaccard, Normalized Weighted Intersection, Dice and Hamming from sets to multisets of tokens and using norms beyond the L1 norm. By "consistent" we mean that the generalized similarity measures reduce to their original set-based prototypes when applied to documents comprised of sets of tokens. Our work, therefore, endows the existing VSM with a new class of similarity metrics, which can be applied to any type of documents comprised of either sets or multisets of tokens.

Application to prototype MMIR problems with national security ties is relevant to Sandia's mission. Two tasks which arise in many national security contexts, entity resolution and attribution, drive this research. Our work resulted in a mathematically precise definition of the entity resolution problem based on the notion of an equivalence class generated by a given entity. Our definition formalizes the entity resolution problem and removes the ambiguity inherent in empirical, ad hoc definitions. This, in turn, reduces the ambiguity in the design of solution approaches for the entity resolution problem.

Successful completion of this project requires resolution of many mathematical and algorithmic challenges. The potential payoff and impact on Sandia's mission are significant and far-reaching. Our research in approximation of the reference optimization problem can lead to new efficient optimization algorithms. The project will leverage Sandia's investment in advanced optimization algorithms and will drive their further development, providing impact on mission critical capabilities. Ongoing collaboration with other Sandians can lead to application of our MMIR framework to the problem of estimation of sentiment in social media content. The pursued research collaboration with other Sandians can lead to utilization of the similarity measures and algorithms developed in this project into the Citrus text-processing environment. In so doing, the research will provide Sandia with MMIR capabilities that support its national security mission and enable future growth in this area.

Coaxial Microwave Neutron Interrogation Source
154763

Year 1 of 3
Principal Investigator: W. C. Johnson

Project Purpose:
Active neutron interrogation has been demonstrated to be an effective method of detecting special nuclear material (SNM), specifically highly enriched uranium. When the neutrons interact with SNM, they induce fission resulting in the emission of neutrons and gammas that may then be detected. Current neutron generation technologies have certain intrinsic limitations, mainly related to the ion source, that lead to high voltage breakdown, excessive power consumption, and shortened operational lifetime. This project explores a revolutionary new type of sealed neutron source based on a coaxial-type microwave ion source that facilitates miniaturization, low-pressure pulsed-mode operation, long lifetime, and high neutron output. Such technology could have widespread national security applications for many ongoing government funded efforts, such as DOE nuclear nonproliferation and radiological source replacement, DHS nuclear detection, and DoD nuclear material locating and tracking.

Summary of Accomplishments:
We have written simulation software to model kinematic distributions of electrons in electron cyclotron resonance (ECR) and have produced tertiary particles in order to optimize design of the device under construction. A comparison of the coaxial dipole plasma source used in this project has been made to the more conventional “magnetic-bottle” ECR ion source via simulation studies. A test stand configuration of the device has been constructed and demonstrated to produce plasma with argon and hydrogen gas; plasma properties were shown to be consistent with results expected from simulation. We have made progress in using results of plasma source simulations to interface to ion extraction and acceleration simulation software being developed in order to allow design and optimization of ion extraction electrodes and acceleration mechanism.

Significance:
DOE, DHS/DNDO (Defense Nuclear Detection Office), and DoD/DTRA (Defense Threat Reduction Agency) have great interest in the detection of fissile materials and nonproliferation efforts. Because the range of detection using passive techniques is limited, all these agencies are interested in active interrogation technologies. Sandia is currently leading the research in nuclear reaction-based systems and is actively pursuing the design of both neutron and gamma generators for active interrogation. An interrogation technology that is man-portable and provides high neutron output offers the capability for examining suspicious containers in remote locations where equipment currently does not exist.

Development of Large Area Geiger-Mode Avalanche Photodiodes
154936

Year 1 of 3
Principal Investigator: S. Soisson

Project Purpose:
There has been an increase in the demand for unattended and remote monitoring systems for many nonproliferation applications, such as the safeguarding of nuclear materials. The increased need for these systems has been prompted by the increase in the number of facilities to be monitored and by the need to maintain continuous inspection in some facilities. Many of the inspection systems used for the monitoring of nuclear materials use radiation detectors based on scintillators and photomultiplier tubes (PMTs). If one is to use these radiation detectors in continuous, unattended scenarios, one must consider their power requirements. While PMTs are used due to their high gain with a large active area and geometrical coverage, they do pose a problem due to their large power requirement for active, continuous measurements. It is of interest to develop a technology which has a lower power requirement but delivers the same photon sensitivity as the PMT. Studies in silicon avalanche photodiodes operated in Geiger-mode (G-APD) with many pixels, show promise for an effective PMT replacement in safeguard situations. The G-APD shows similarities to the PMT but offers the advantage of having a low power requirement and greater robustness. However, the size of available G-APDs is only 6 mm^2. This is not appropriate for replacing a PMT when large active areas are needed. We propose a two-year project to study the feasibility of the development of a large area G-APD for a PMT replacement. This development is high-risk, as many of the fundamental parameters are not well understood for a G-APD. It is believed that these parameters could give insight into why the current limitation in size for a G-APD is around 10 mm^2. Utilization of tightly coupled microsystems/CMOS (complementary metal oxide semiconductor) processing techniques at the Microsystems and Engineering Sciences Application (MESA) facility to create unique physical structures are expected to enable new detector operation/isolation approaches that will alleviate the limitations observed in existing devices.

Summary of Accomplishments:
The first milestone presented in the lifecycle plan is to have the first interim modeling of a G-APD completed with the help of the staff at the MESA facility. This is on schedule. Learning and understanding of the Sentaurus semiconductor modeling software has been completed as of June 2011. Two prototype devices have been chosen for in-depth modeling purposes. The first is a p-on-n structure. This has been chosen to enhance the efficiency of collection of light in the ultraviolet (UV)-Visable range over that of an n-on-p structure. The second is built on a lightly doped p-region with 2 highly doped regions to reach a fully reversed biased state. Both of these designs will be built on a silicon-on-insulator (SOI) wafer. The oxide layer in an SOI wafer has been reported to reduce the parasitic capacitance of the handle layer in some semiconductor devices. The size of each micro-cell has been chosen to be 32 micrometers square. Between each active area, there will be a trench for optical isolation between active areas. These designs will be refined in accordance with the manufacturing capability of the MESA facility. The prototype designs are ahead of schedule and were delivered to MESA at the end of July. The process flow and masking for the fabrication process is currently being completed by the MESA staff. However, it is unlikely given the MESA fabrication schedule that prototypes will be delivered ahead of schedule.

Significance:
Radiation detection is one of the common requirements of a number of DOE, NNSA, and DHS missions. Advancements in this area will substantially enhance the ability of numerous organizations to accomplish their national security missions.

Within the DOE, one of the goals within their national security mission is to provide technical assistance to secure nuclear weapons, special nuclear materials (SNM), and radiological materials around the world. We support this goal by researching innovative solutions for continuous remote monitoring of nuclear materials.

Characterization of Atmospheric Ionization Techniques for the Identification of New Chemical Signatures from Homemade Explosives in Complex Matrices
156400

Year 1 of 3
Principal Investigator: J. M. Hochrein

Project Purpose:
Currently, there is high demand for analytical capabilities that can rapidly identify weapons of mass destruction, including home-made-explosives (HME), chemical, and biological agents, and at the same time obtain forensic signatures quickly, easily, and in a portable fashion. Current ion mobility (IMS) methods, including those used in airports, are very limited in their effectiveness for these targets due to their limited resolution, ionization, and lack of biological detection. Desorption Electrospray Ionization (DESI) and other atmospheric ionization techniques coupled with mass spectrometry offer distinct advantages over traditional detection systems because of the extremely diverse range of detectable compounds, vastly improved specificity, high throughput, fieldability, and little to no sample preparation.

Although DESI has been demonstrated on some target compounds, significant technical challenges and opportunities associated with the method exist. First, there are many operational parameters that need to be optimized, such as solvent selection, ionization energies, surface material selection, and identification and reduction of background contaminants. Second, many of the target compounds are analyzed as "neat" samples in very controlled environments under optimum conditions that are often very different from those in the field. In addition, many analytes of interest, including HME precursors and HME residues, have not been investigated to determine whether they are amenable to ambient detection.

This research will focus on enhancing scientific understanding of DESI and other atmospheric ionization techniques to address two challenging problems that currently exist in national security: 1) detection of a wide variety of HME materials in complex matrices including transport containers, soil, biological metabolites and post-detonation scenarios and 2) identification of new chemical signatures associated with HME production and investigation of the detection of HME residues to identify unique signatures which will enhance the specificity of detection. Information on specific ions that can identify particular HME can then be used to enhance the effectiveness of existing technologies including IMS and differential ion mobility.

Summary of Accomplishments:
Accomplishments completed in FY 2011
1. A comprehensive literature review was performed.
2. DESI instrumentation has been purchased, installed and tested.
3. HME materials have been received and have been analyzed using DESI combined with high-resolution mass spectrometry.
4. Imaging of chemical signatures was demonstrated using DESI.
5. Optimization of solvent systems and ionization parameters has been tested and improvements in detection have been realized. Additional studies are under way to learn how to further optimize the parameters for trace level detection in complex matrices.
6. Three oral presentations were given in FY 2011. One was presented at the Sandia Aviation and Explosives Security Symposium and two were presented at the Joint Working Group 28 meeting at Y-12.

Significance:
Unique applications exist at Sandia, offering opportunities to explore and utilize DESI to provide new and faster information to solve scientific problems and to protect our country, citizens, and stockpile from harmful acts while addressing the strategic plans of DOE, DHS, and other federal agencies. Advances in HME characterization and detection are of extreme importance to DHS.

Explosively Driven High-Power Microwave Source
141590

Year 2 of 2
Principal Investigator: L. R. Shapnek

Project Purpose:
Electromagnetic pulses of proper frequency and amplitude have demonstrated the ability to disrupt, disable, or destroy electronic systems. These systems can generate extraordinarily high effective radiated power (ERP) but typically require large power supplies, such as capacitor-based Marx Banks that are difficult to miniaturize. An efficiently designed single-shot system that leverages the greater energy density of explosives for its power source, such as a Flux Compression Generator (FCG), has the potential to deliver the same power to an antenna in a smaller system volume.

A general concept design for an FCG-based high-powered microwave (HPM) source is relatively simple. It consists of an FCG, an impedance-matching section, and an antenna. The great advantage of such a system over conventional HPM sources is that the energy stored in explosives (~10 x 10^3 J/cc) is much higher (50,000 times higher) than the energy density stored in high-voltage, low-impedance capacitors (0.2 J/cc). The great disadvantage of FCG-based HPM devices is that the FCGs themselves have sub-Ω source impedance, and the RF antenna's impedance is >100 Ω, mostly negating the gains of having higher energy density. This project demonstrates that a properly designed impedance-matching section for an FCG-based HPM device can be designed and applied to a system to generate meaningful RF output.

The availability of legacy FCGs allowed us to take on this project with relatively low risk in the FCG itself. This, along with our extensive experience in the design of radio-frequency pulse generators, allowed realistic project goals. Because the FCG design is fixed, efficient handling of the electrical power within the transformer and Inductive Capacitive Oscillator (LCO) sections were the high-risk area of this project.

Summary of Accomplishments:
We reestablished FCG operational capability within Sandia. We used new magnetic modeling capability to design a pulsed high-voltage transformer and used other modeling to guide and iterate a system that accommodates the complex FCG-Transformer-LCO electrical energy interactions. This work culminated in demonstrating an explosively driven HPM source that generated electrical field strengths in the regions of interest to our collaborators.

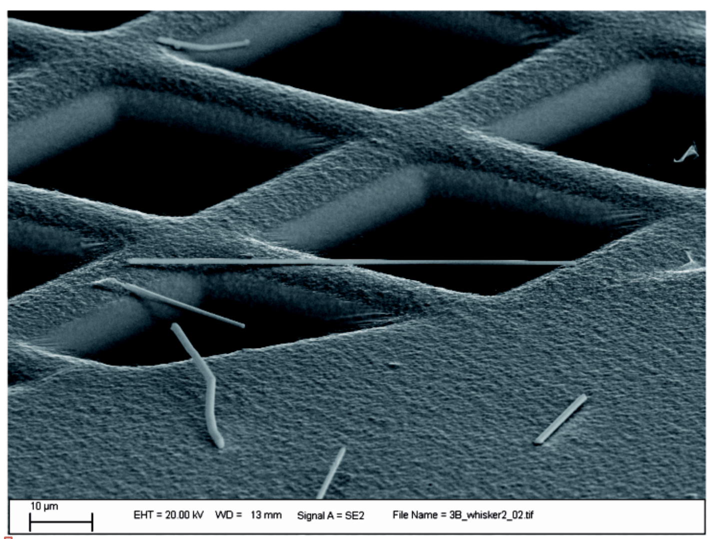
Significance:
The successful demonstration of an explosively driven HPM source positions Sandia to provide a leadership role for addressing the many areas where there is a pressing security need for such a solution. Several applications will directly benefit from this compact power supply design experience; potential applications for this technology cover many possibilities in countering threats. We are in considering future projects using this technology, and we believe that follow-on successes will generate yet more applications.

NUCLEAR WEAPONS INVESTMENT AREA

From fundamental studies into novel material combinations underlying better sensors and actuators, to more immediately employable sensors for monitoring the environment of weapon components, to improved nuclear weapons communications architectures, the projects in this investment area all aim to provide better, more reliable methods of stockpile stewardship, with potential impacts to related mission areas (such as advanced battery construction and the role of the hydrogen economy in non-fossil-fuel energy generation).

Understanding and Predicting Metallic Whisker Growth and its Effect on Reliability
Project 130800

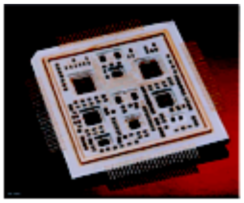
As the electronics industry continues to move toward lead-free components, engineers are encountering new issues on the microscale. This project is studying one of those circumstances, the occurrence of tin "whiskers" on the lead-free surfaces of tin-coated electronics, a phenomenon that was more rare when the surfaces were composed of a tin-lead alloy. This is problematic in that such whiskers — thin extensions of tin metal — can carry electrical current, thus raising the possibility of shorting failures between conductors. The project is characterizing the phenomenon using tools such as electron backscatter diffraction (EBSD), Focused-Ion Beam (FIB), electron microscopy, confocal microscopy and others, studying whisker growth kinetics as a function of temperature. Additionally, computational modeling is being employed to predict whisker nucleation density and growth rate, thereby assisting in establishing the important parameters that determine whisker formation, so that it can be understood — ultimately well enough so that it can be controlled or eliminated. For example ESBD revealed that almost all whiskers are single crystals. The project team is collaborating with scientists at North Carolina State University to attempt to improve the accuracy and predictive value of its models. Growth rate and preferred growth direction are much better understood because of this project's investigations.



Scanning electron micrograph of tin whiskers forming on a metal grid

Localized Temperature Stable Dielectrics for Low Temperature Co-Fired Ceramic
Project 148900

Key dielectric materials for electronic chips integrating a variety of components — and with mission applications in radar fuze, SAR (Synthetic Aperture RADAR) and other arenas — low-temperature



cofired ceramic(LTCC) systems comprise packaging materials for multilayered chip modules that have been important in the growth of wireless communication over the last decade. They are traditionally manufactured in a fashion that yields a temperature coefficient of resonant frequency (T_f) in the range –40 to –70 ppm/°C. This parameter, a key device property affecting device bandwidth would more-desirably have a value at or near zero, and schemes to compensate for its deviation from zero have been costly and complex, less-than-ideal from the energy-efficiency perspective. This project's novel approach has been to develop *local* compensatory solutions to adjust T_f, examining an array of materials that can be incorporated into the structure in the key areas where resonators are located, thereby effecting what a "localized T_f compensation." This is theoretically possible, given that the electromagnetic field of resonator embedded inside a LTCC does not distribute throughout the entire module, but is rather locally confined. Challenges associated with this approach are both chemical (such as interdiffusion of molecular species) and physical (such as material shrinkage).

A Tf compensating material has been developed based on its high sintered density and its high temperature coefficient of capacitance. A patent is pending. For a double layer of this material on both sides of a stripline ring resonator the T_f approached 0ppm/°C. These results demonstrate the feasibility of localized T_f compensation.

Nuclear Weapons Investment Area

Field and Charge Penetration by Lightning Burn-through
130793

Year 3 of 3
Principal Investigator: L. K. Warne

Project Purpose:
The continuing current component of the lightning environment is capable of breaching many system exteriors. However, the breach takes the form of a small hole which is surrounded by hot plasma. Because lightning is made up of large amplitude return strokes separated by these continuing current intervals, there has always been a concern that such a breach will leave interior cables or other components in proximity to the hole subject to coupling. One valuable measurement was made in 1994 on a cable behind a burn-through hole subjected to a return stroke, which yielded relatively low levels of induced voltage and current. But it is not known whether the setup in this measurement captured extreme levels or what physical principles were at work to prevent more extreme levels from being observed.

We proposed in this project to examine, both theoretically and experimentally, the physical principles at work in the transfer of field and charge through the hole. The goal is to provide a rigorous basis for understanding levels of induced voltages and currents. Such an understanding will allow a more realistic assessment of this environment (perhaps in some cases even allowing it to be dismissed).

Summary of Accomplishments:
1. Identified four fundamental penetration mechanisms in lightning burn-through of metallic barriers: a) indirect electric, b) indirect magnetic, c) discharges to the interior, d) plasma conduction.
2. Added severe continuing current and high-speed photography to original burn-through experiments. Going from nominal continuing current durations and charge transfer levels between return strokes (used in the original test) to severe one percentile levels resulted in fast-rising currents of up to one kiloampere and voltages up to one kilovolt.
3. Developed new test method (starter wire) to address multiple return strokes. The starter wire initiation of the experiment allowed us to use two severe return strokes with one-percentile levels of action to enlarge the hole and couple to the interior.
4. Developed indirect coupling models which compared favorably to low-level experiments. These indirect models identified the important features of the burn-through hole which control the levels of penetration. The low-level Velonex and pulse arrested spark discharge (PASD) pulsers provided clean experimental comparisons without discharges.
5. Performed discharge threshold simulations to interior cable which compared favorably with medium-level experiments. The predictions of spark discharge by using ionization thresholds combined with requirements of streamer propagation in nonuniform field gaps compared favorably with spark voltage data gathered using the medium-level pulser.
6. Developed probes to investigate plasma current distribution which compared favorably to gas discharge models. Two types of probes were developed to observe the radial current distributions in the return stroke plasma on a metallic surface. These results agreed with analytical Braginskii model predictions as well as Alegra simulations on a surface.
7. Developed plasma conduction and impedance models which compared favorably with high-level experiments. Predictions of voltage drops along interior plasma channels from the cable to chassis agreed with high-level lightning experiments.
8. Publishing a paper in IEEE *Transactions on Plasma Science*.

Significance:

The understanding and models of the energy transfer process involved in lightning burn-through to be developed in this project will provide a quantitative basis on which to make safety assessments about this penetration, which is relevant for many existing systems. The results of this project will also advance our understanding of nonlinear energy transfer processes interior to a system.

MEMS-Based Non-Volatile Memory Technology
130794

Year 3 of 3
Principal Investigator: M. Baker

Project Purpose:
Electrical non-volatile memory (NVM) technologies are currently used for several purposes in nuclear weapons systems. Each application has different requirements for the number of bits stored, the speed and power required to read and write, the duration of storage without power, erasing/rewriting without remnants of previous storage, and radiation hardness. The perfect NVM technology does not exist, so compromises are made in system design and operation.

We proposed to create a microelectromechanical system (MEMS)-based NVM that would enable new system designs by overcoming some of the weaknesses in current memory technologies. Data would be represented by the position of a buckled beam (e.g., up or down for 1 or 0, respectively). Electrodes above and below would electrostatically actuate each beam and capacitively sense the position. We believe that this scheme has inherent advantages in radiation hardness, duration of storage, and in completely erasing previous data. Further, this technique should be highly reliable because it involves no rubbing or contacting surfaces.

Successful development of a mechanical NVM device requires the development and integration of several key elements including the fabrication of very thin gaps and thin beams with highly controlled residual stress, the design of an integrated circuit for capacitive sensing and actuation, the packaged integration of the MEMS die with the integrated circuit, and the material science studies required to demonstrate lifetime and reliability of the mechanical beam element. Of these technical challenges, the beam fabrication and reliability are the largest and push the state of the art in thin-film mechanical MEMS. Understanding the evolution of stress during the fabrication process and controlling this stress in a polysilicon beam is an active area of research, and this is a high-risk aspect of this project.

Summary of Accomplishments:
We have demonstrated the successful actuation and measurement of a single-bit MEMS polysilicon buckled beam non-volatile memory element. However, when actuated, the beam contacts and sticks to the actuation electrodes, increasing the actuation voltage and negatively impacting reliability. A significant effort was put into resolving this contact and adhesion problem, with a successful solution found by using short-pulsed actuation tuned to the dynamics of the buckled beam. Once this solution was found, it became apparent that stress gradient and non-idealities in the beam anchors caused an asymmetry in the buckling behavior. Because of this, most of the beam designs do not have a second stable position. Independent control of both the average stress and the stress gradient would be required to resolve this issue, and this has proven very challenging for thin polysilicon beams.

We have also developed a process for flip-chip bonding two die together using an indium-gold liquid-phase bond. This would allow the MEMS die to be bonded to a controlling application-specific integrated circuit (ASIC) with a reliable high count interconnect system. We have demonstrated 100% yield on a 252 bond-pad array using this approach.

Finally, we have deepened our understanding of stress and deformation of silicon-on-insulator (SOI) wafers used in high-temperature MEMS processing. There is a desire to use these wafers with subsequent thin film depositions, but in past efforts the required high-temperature anneals caused the SOI wafers to permanently buckle into a saddle shape, rendering them un-manageable by lithography equipment. We now believe that this is due to the level of interstitial oxygen present in the starting SOI wafer, and its effect on dislocation motion. Our enhanced understanding of this problem, obtained through experiment, will help future programs and will enable the use of SOI starting wafers in MEMS processing.

Significance:
This project ties directly to Sandia's national security mission in the area of nuclear weapons security and technology development. The advantages provided by this new memory technology would enable new system architectures that would improve upon existing solutions.

Novel Dielectrics with Engineered Thermal Weaklink
130797

Year 3 of 3
Principal Investigator: S. M. Dirk

Project Purpose:
The nuclear safety criteria for a thermal weaklink are that it must fail "predictably and irreversibly." We have engineered a dielectric system that has a known, predictable failure mechanism built right into the polymer backbone that will fail predictably and irreversibly in a designed manner and at a designed temperature. This dielectric system fails by its permanent transformation to a semi-conducting polymer at a specified temperature, which significantly diminishes the capacitor's ability to store the necessary charge. In addition, it is projected that, under normal environment operation, the proposed polymer will provide a significant current leakage path, in effect creating a robust/intrinsic bleed path (in situ bleeder-resistor) for removing stored charge when power is removed.

This work represents the first utilization of the thermo-switchable properties of precursor poly(p-phenylene vinylenes) (PPV's) for an application. The application (serving as a thermal weaklink in capacitors) has important safety ramifications for capacitor devices in the stockpile and in general. We show that these polymers have better dielectric properties than commercially available non-fluorinated polymer dielectrics. Through the synthesis of several new precursor polymers, the thermo-conversion temperatures of these materials are shown to be directly related to the stability of the leaving group, which is an important finding for the general processing of these types of materials for polymer based electronics. This work represents the development of a truly "first principles" based thermal weaklink capacitor.

Summary of Accomplishments:
We built on our successful demonstration of the first thermally switchable polymer dielectric system (from dielectric to conducting polymer). In that demonstration, we determined that, after the thermal transformation, the capacitance values typically dropped more than 80% while the dissipation factor increased ~75 times, clearly demonstrating irreversible capacitor failure and showing the ability of these systems to serve as weak-link dielectrics. In FY 2011, we synthesized and evaluated alternate polymers with improved properties. Several new xanthate precursor polymers were evaluated and determined that, while these materials are easily synthetically accessible, have good electrical properties at room temperature, and conjugate to form conducting polymers at high temperatures, they do not perform well as dielectrics at elevated temperatures because the polymers have low glass transition (T_g) temperatures. Based on these initial observations, we designed several alternate high T_g xanthate polymer systems to improve the thermal characteristics, which will enable these materials to function as weaklink dielectrics.

It was determined that some of the switchable dielectrics were very hydrophilic. In these polymers, the relative permittivity and dissipation factor changed with humidity. We further identified switchable polymers that were hydrophobic. The hydrophobic materials did not change as the humidity changed.

Having a very good understanding of the materials properties of the switchable dielectrics led us to focus on the fabrication of a hybrid capacitor structure. The hybrid structure consisted mainly of Mylar with a small portion based on the novel thermally switchable materials. The hybrid system will fail in a controlled way via the change from non-conjugated material to conjugated material.

Furthermore, we successfully demonstrated that the xanthate-based PPV precursor polymers can be photopatterned to create conjugated structures with feature sizes as small as 1 μm. This very novel work led to a patent being granted only eight months after patent submission.

Significance:

This work represents the following significant accomplishments: 1) it illustrates the first utilization of the thermo-switchable properties of precursor PPV for an application, 2) the application has important safety ramifications for capacitors in general because the capacitors will irreversibly shut down in the event of a fire or overheating, 3) we have shown that, under normal operating conditions, these polymers have better dielectric properties than commercially available Mylar and other non-fluorinated polymer dielectrics, 4) through the synthesis of several new precursor polymers, the thermoconversion temperatures of these materials are shown to be directly related to the stability of the leaving groups, which allows the failure temperature to be preset, 5) the ability to lower the thermoconversion temperature is an important finding for the general processing of semiconducting polymer-based electronics because it increases the number of materials that can be coprocessed in a device without degradation of the constituent materials, 6) the materials developed under this project are useful as thermally-induced small-molecule delivery devices, 7) we have demonstrated photopatterning of the PPV precursor materials as a direct method to pattern conjugated polymers, 8) materials developed under this project are very useful in optical applications requiring switchable index of refraction materials and 9) this represents the development of a truly "first-principles-based" thermal weaklink capacitor.

Refereed Communications:

R.S. Johnson, P.S. Finnegan, D.R. Wheeler, and S.M. Dirk, “Photopatterning poly(p-phenylenevinylene) from Xanthate Precursor Polymers,” *Chemical Communications*, vol. 47, pp. 3936-3938, February 2011.

Signal Processing Techniques for Communication Security
130798

Year 3 of 3
Principal Investigator: R. J. Punnoose

Project Purpose:
Wireless communication can enable new logistics and tracking applications for the storage and transport of sensitive material in containers. This will provide accurate real-time inventory, prevent theft, and decrease the cost of protecting this material. Also, environmental conditions that will help in predicting the aging of materials can be monitored during storage and transport. Since radio communication occurs over an open broadcast medium, security is an issue.

The goal of this project is to use time-reversal electromagnetics to provide inherent wireless communication security at the physical layer by focusing the communication signal at the receiver. This technique has potential to provide low-probability-of intercept, low-probability-of-detection (LPI/LPD) characteristics to radio communication, independent of any spread-spectrum modulation.

This project aims to develop a differentiating technology to increase the safety and security of sensitive material. The focusing ability of an antenna depends on its size and is limited by the Rayleigh diffraction limit. Recently, experimental proof-of-concept articles showed that it is possible to focus beyond the diffraction limit in a spatially cluttered environment using time-reversal techniques.

Time-reversal techniques have the following properties: 1) background clutter is beneficially used to create a large virtual aperture, 2) increased focusing ability, 3) no need for knowledge of receiver position, and 4) no need for line-of-sight. For practical application, it is imperative to determine the relationship between focusing ability and: 1) number of antennas and their spacing and 2) the degree of clutter. For security applications, it is also desirable to simultaneously detect and suppress potential threats.

The objective of this proposal is to: 1) characterize the impact of the factors listed above on the ability to focus signals on a target, 2) selectively detect and reject hostile signals using time reversal techniques, and 3) simultaneously focus and null the signal at desired/undesired locations.

Summary of Accomplishments:
We have explored the performance of time reversal, focusing in a variety of simulated environments. We have developed new algorithms to simultaneously focus at a location while nulling at a different location. We have experimentally verified these techniques in a realistic cluttered lab environment.

Significance:
This work supports DOE's Defense Strategic Goals by enhancing the security of sensitive material transported in containers. It can also support military technologies and remote sensing.
In addition to this, this technique can be useful for tagging and tracking, which have asymmetric communication needs. Time reversal processing can be applied at the tag reader to focus the energy at the tag, which has very little processing power. This will eliminate the need for the tag to perform power-hungry equalization. This technique can, therefore, be of use in the Intelligence, Surveillance, and Reconnaissance (ISR) area.

Solid State Neutron Sources
130799

Year 3 of 3

Principal Investigator: J. M. Elizondo-Decanini

Project Purpose:
We proposed to accomplish the following objectives:
1. Use solid state and microelectronic technology to produce a neutron generator.
2. Demonstrate neutron production using a millimeter printed-circuit flat design.
3. Demonstrate computer-chip-sized neutron sources.

Summary of Accomplishments:
During the past year of this project, we have made the following key accomplishments:
1. Demonstrated deuterium-ion sources in the millimeter-size range using ceramic substrates.
2. Demonstrated in excess of 200 shots.
3. Demonstrated deuterium-ion sources in the µm size range.
4. Demonstrated in excess of 100 shots.
5. Demonstrated neutron production using surface-printed components in the millimeter size range.
6. Demonstrated deuterated ion source with tritium-loaded target.
7. Two patent applications have been filed (mm size chip, and radial chip).
8. Six additional invention disclosures were filed based on ideas inspired by this work.
9. Two journal papers are in preparation.
10. Technology transfer has been initiated for medical applications.

Significance:
The proposed work represents the state-of-the-art in neutron generator technology; it matches the DOE requirements for innovation enabling research and creation of dominance in key scientific fields that will transform the 21st century global economy. We have demonstrated and opened the door for future all-solid-state neutron generators and very large output compact sources. This work represents a transformational approach to neutron-generator fabrication and applications. This work can make medical applications for patient-portable neutron-capture therapy a realistic commercial venture. This work also enables replacement of active sources in other applications such as well logging and ultra-high-neutron-output sources.

Understanding and Predicting Metallic Whisker Growth and its Effect on Reliability
130800

Year 3 of 3
Principal Investigator: D. F. Susan

Project Purpose:
Tin (Sn) whiskers are conductive Sn filaments that grow from Sn-plated surfaces, such as surface finishes on electronic packages. The phenomenon of Sn whiskering has become a major concern in recent years due to requirements for lead (Pb)-free soldering and surface finishes in commercial electronics. At Sandia, Sn whiskers are a reliability concern due to increased use of commercial off-the-shelf (COTS) parts, possible future requirements for Pb-free solders and surface finishes in high-reliability microelectronics, and the transition of Sandia's electronics supply chain to Pb-free processes. In general, pure Sn finishes are more prone to whisker growth than their Sn-Pb counterparts, and high profile failures due to whisker formation (causing short circuits) in space applications have been documented. Despite the long history of Sn-whisker research and the recently renewed interest in this topic, a generally accepted explanation of the whisker-growth mechanism has never been developed. The purpose of this project is to develop an understanding of the underlying mechanisms that control the nucleation and growth of Sn whiskers. The experimental part of this work includes the effects of critical variables such as Sn microstructure, grain orientation, temperature, and stress on the propensity for Sn whisker formation. Concurrently, computational modeling, which is based on molecular dynamics techniques for describing stress-driven mass transport processes, will be developed to predict transport mechanisms feeding whisker development. The modeling will utilize realistic atomistic simulations based in part on the detailed characterization obtained in the experimental portion of this work.

Summary of Accomplishments:
We have continued to present our results at scientific conferences, including two presentations at the 5th Annual International Tin Whisker Symposium, as well as a conference paper and presentation at Microscopy and Microanalysis 2011. As a result of this project, Sandia is firmly established in the Sn-whisker research community. We are actively preparing several peer-review journal publications to be published in the coming year.

Over the life of this project, we developed a reliable method for producing Sn-plated samples that form Sn whiskers. The process employs an alkaline stannate bath, operated at room temperature or higher, with a rotating disk electrode technique. The best conditions for plating Sn-whisker samples was determined to be -0.2 to -20mA current in chronopotentiometry (CP) mode or ï 1500 to ï 2500mV in chronoamperometry (CA) mode at 70 °C, 1000 rpm rotation speed, for plating times ranging from 5 to 40 minutes. The coatings are typically about 1 micron thick on a pure Cu substrate. The development of these plating processes allows us to study Sn-whisker growth using electron microscopy, x-ray diffraction, and other advanced characterization techniques.

We have fully characterized the crystallography of Sn whiskers. Through advanced electron backscatter diffraction (EBSD) and x-ray diffraction (XRD), we have statistically determined the crystallographic growth directions of over 100 whiskers on several samples. We have shown that there is no correlation between the whisker growth direction and the overall texture of the film, at least for our weakly textured films. This type of thorough analysis of whisker crystallography has not been previously reported anywhere in the literature.

We have also characterized Sn-whisker growth kinetics at room temperature as well as the kink morphology during whisker growth. Importantly, we have observed that the kinking process is associated with a slowdown or complete stoppage of whisker growth.

Significance:
Tin whiskers represent a challenging scientific field of study. The phenomenon of Sn whiskering has been known for over 50 years, but there is still no universally accepted whisker-growth mechanism. This work exercised Sandia's unique materials characterization capabilities and is maintaining our expertise in this area. Through advanced scanning electron microscopy (SEM), EBSD, and XRD characterization techniques, we have generated data that no one else has reported in the literature. We have determined the crystallography of tin whiskers and compared it to the overall crystallographic texture of Sn films. In general, Sn whiskers grow in low-index directions: <001>, <100>, <101>, and <111>. These directions correspond to the normal to the following crystallographic planes in tetragonal Sn: (001), (100), ~(301), and ~(331). The crystallography results represent careful analyses of over 100 whiskers. The crystallography of Sn whiskers is not necessarily related to the overall texture of the film (at least for weakly textured films). It follows that the crystallography is not related to the whisker physical growth angle in a simple way. That is, whiskers of one type, say <001>, can grow at many different angles off of the Sn surface. All of these discoveries show the complexity of the Sn-whisker phenomenon and the need for further study in this area. In particular, EBSD crystallographic analysis of the grains surrounding a whisker will be important in understanding the grain boundaries that support Sn diffusion and grain boundary sliding associated with whisker growth.

A thorough understanding of Sn-whisker growth could lead to techniques for engineering Sn films that reduce or eliminate whisker growth. Indeed, in this project we have deposited Sn films under a variety of conditions that show no whisker growth. For example, pulse plating changes the Sn microstructure in such a way so as to suppress whisker growth; we have not observed whiskers in pulse-plated films. In addition, by understanding the crystallography of Sn whiskers, we are exploring ways to deposit Sn in specific crystallographic orientations. For example, depositing a highly textured <100> film should suppress <001> whisker formation. It is possible to predict which whisker types will be suppressed for a given Sn film texture. These experiments involve plating Sn on single-crystal Sn of selected orientations as well as depositing Sn on highly oriented Au thin films. These approaches to Sn-whisker mitigation have only been made possible by the understanding of Sn-whisker crystallography gained in this research.

Tin whiskering is of increasing concern for nuclear weapon, satellites, and homeland security applications. As such, it is a very relevant research field for Sandia, considering our emphasis on high reliability microelectronics, the shift toward commercial off-the-shelf (COTS) parts, possible future Pb-free requirements, and the shift of the supplier base to Pb-free processes. Furthermore, it will be possible to apply the techniques and modeling tools developed in this work to other, yet unforeseen, materials problems involving thin films, diffusion, and residual stress. The underlying motivation for research is the move toward Pb-free COTS parts and likely future requirements for Pb-free electronics.

Vapor-Phase Lubrication for Advanced Surety Components
130801

Year 3 of 3
Principal Investigator: M. T. Dugger

Project Purpose:
Future weapon architectures will employ surety components with smaller dimensions than legacy components. These may use materials ranging from engineering alloys to silicon. Materials selected for manufacturability, strength, etc., frequently exhibit poor friction and wear properties, necessitating lubricants. Conventional solid lubricants oxidize, increasing friction and wear and uncertainty in performance with age. Depositing lubricants uniformly without damage is difficult with current methods and impossible with shrinking component dimensions. Recent alternatives such as impingement MoS_2 and diamond-like carbon have met current life extension program requirements, but they will be difficult to deposit uniformly with controlled chemistry and adhesion on smaller parts without damaging them. The elimination of hazardous solvents has created a critical need for new stainless-steel-bearing lubricants.

The goal of this project is to develop a completely new paradigm for surety component lubrication, known as Vapor Phase Lubrication (VPL), that will provide a low friction film of molecular dimensions is self-healing, and forms automatically during sliding on small parts of complex shape. The underlying scientific discovery has already been demonstrated by the investigator through an invention disclosure. VPL is based on a reaction between gas phase molecules and the surface that forms a lubricant film only at contact locations. This approach has shown a 10,000-fold increase in operating life of silicon micromachines without failure, and recent experiments indicate that VPL is also effective on stainless steel. The use of VPL in weapon components requires understanding the reaction mechanisms, optimizing vapor chemistry for different substrates, developing vapor delivery strategies compatible with weapon components, investigating aging of the resulting film, and determining the compatibility of the vapor with other component materials. Significant development, with relatively high risk, is required to mature VPL for the range of weapon operating temperatures required and to create vapor delivery approaches.

Summary of Accomplishments:
The vapor-phase lubrication of silicon and engineering alloys was investigated in this project. Fundamental studies of the chemical interaction of molecules with metal and metal-oxide surfaces showed that, in addition to the hydroxyl termination in linear alcohols, surface passivation could be achieved with acid, olefin, and methyl terminations as well. The formation of complex cyclic hydrocarbon compounds during tribological contact was first observed in time-of-flight, secondary ion mass spectrometry (SIMS) data and was confirmed using fluorescence microscopy and Raman spectroscopy. This is a significant finding independent of the use of these molecules as lubricants, since the processes required to synthesize cyclic compounds via other routes typically require much larger energy input. Several approaches for delivering vapor species inside sealed volumes were developed. An "on-demand" approach was thoroughly investigated and consists of a specially synthesized polymer that, when heated, reacts to produce the desired alcohol species. A packaging process using this material was developed and exercised to produce hermetic packages containing microelectromechanical system (MEMS) devices and the vapor phase lubrication source for in situ delivery.

Vapor phase lubrication of conventional stronglinks was investigated using an electrical contact prototype stronglink. Compared to an nonlubricated device, a device lubricated with pentanol at 50% of the saturation pressure at 25 ˚C (about 2600 ppm) exhibited improved performance characteristics, including the complete absence of wear debris formation and more consistent electrical contact resistance. A study of the compatibility of materials with pentanol vapor lubricant revealed that some epoxies used for staking threaded joints exhibited significant solvent uptake. Other polymers are available that would avoid the interaction with pentanol so that a component can be designed with vapor lubrication and compatible polymers.

Significance:
Vapor-phase-lubrication technology has been significantly matured toward application in weapon electromechanical devices. The technology has been demonstrated to improve the friction and wear characteristics of conventional stronglinks that use engineering alloys, in addition to dramatically extending the operating life of silicon micromachines compared to other lubrication strategies. There were some interactions of the lubricant vapor with polymeric materials in conventional stronglinks that had a negative impact on those materials. However, there are available alternative polymers that would avoid these interactions. The creation of complex cyclic hydrocarbons during sliding in the presence of alcohol vapor represents a new innovation that was not central to the use of these molecules as lubricants, but may have other applications in efficient synthesis of cyclic compounds. The need to deliver the vapor species in a sealed volume on demand led to the development of new polymer precursors that liberate the desired alcohol when heated. These materials were used in a newly developed packaging process for silicon microsystems. The on-demand delivery approach provides one solution to the limitations of the operating temperature range of the vapor-lubrication process. Previously, if the desired vapor concentration were sealed into the operating volume during manufacturing, the operating temperature range was limited by the need to avoid condensation to liquid phase at low temperature and the need to maintain sufficient vapor pressure for monolayer adsorption at high temperature. The operating temperature range in this “fill and forget” delivery approach is approximately 60 ˚C. With on-demand delivery, two additional electrical feedthroughs are required to deliver power to a heater used to drive reactions in the polymer, and a control system is required to determine how long to heat the polymer. However, this allows pulse heating of the polymer that can be used to control the amount of alcohol evolved. In this way, the appropriate concentration of alcohol can be created for any desired operating temperature.

Refereed Communications:
A.L. Barnette, J.A. Ohlhausen, M.T. Dugger, and S.H. Kim, “Humidity Effects on In Situ Vapor Phase Lubrication with N-Pentanol,” to be published in the *Journal of Microelectromechanical Systems*.

M.T. Dugger, “Tribological Challenges in MEMS and their Mitigation via Vapor Phase Lubrication,” in proceedings of the *Micro- and Nanotechnology Sensors, Systems, and Applications III*, pp. 1-5, 2011.”

Fully Integrated Switchable Filter Banks for Advanced Radar Applications
141688

Year 2 of 2
Principal Investigator: E. R. Crespin

Project Purpose:
Switchable filter banks represent a critical technology gap for realizing the next generation of advanced radar systems. Current radar designs use a number of wideband filters to supply the necessary frequency selectivity, but this is both inefficient (power, cost, size, and component count) and undesirable (more easily jammed, etc.). Radar designs using radio-frequency integrated-circuit (RFIC) technology still require many wideband filters that drive up component count despite the push towards higher levels of integration. Ideally, a radar designer requires a bank of narrowband filters with the ability to switch filters depending on the various radar modes of operation. Microfabricated resonators offer a smaller, more highly integrated filter technology than what is available using traditional bulk or surface acoustic wave (BAW or SAW) techniques. Microresonators can realize arrays of filters from 20 MHz to several GHz on a single chip and can be fully integrated directly over Sandia's CMOS7 technology without altering the CMOS7 fabrication. CMOS7 technology is already being pursued in advanced radar development efforts. This integration ability is fundamental to providing a switchable array of narrowband filters, as microresonators can be fabricated along with the CMOS7 process and integrated with the circuitry for higher reliability and lower component count. With this research, we will learn to design multi-pole, low impedance filters with low loss using microresonator technology.

Also, complementary metal oxide semiconductor (CMOS) switch technology will be scaled for the best performance, and new materials integration techniques will be tested as we fully integrate AlN microresonator technology with CMOS devices.

Summary of Accomplishments:
A fully integrated switchable filter bank had been successfully demonstrated, offering a monolithic solution for what is currently a multi-chip radar application.

The S-band switches had very reasonable insertion loss (~2dB), isolation (25dB) and power handling (0.4W), all of which could be improved with design/layout tweaks and better transmission line modeling, as the switch performance was heavily dependent on layout. This project also developed new RF CMOS7 models from DC to 5GHz, enabling better prediction of device performance which results in less design iterations in the future. The effect of chemical-mechanical polishing (CMP) fill in and around radio frequency (RF) circuitry was found on all switches to varying degrees. More work is required to precisely understand how much and how close the CMP fill can be to RF circuits.

The microresonator filters made significant technological advances. S-band filters were modeled, fabricated, and demonstrated multiple times throughout this project. Insertion loss improved from 9dB to 5.5dB and the reduction of spurs, both in and out of band, also occurred.

The chip and wire integration performed as expected, allowing the full integration to proceed without any foreseeable problems. Monolithic integration was achieved on multiple switch designs, with the best performance on the switch with the most paths (SP4T). The fully integrated switchable filter bank performance, while layout dependent, showed full functionality of the CMOS7 switches and the microresonator filters as well as demonstrated the compatibility of the two technologies.

The ultimate technological goal of this project has been achieved and is a significant accomplishment as this is the first time this has been done at S-band. Along with that major milestone, this was also the first time switches and microresonator filters were demonstrated at S-band. While the monolithic solution is not ready for immediate insertion into nuclear weapons (NW) systems, this project has proven its feasibility.

Significance:

The benefit to Sandia's mission and to nuclear weapons of integrating RF switches and filter banks is increased reliability, in part by decreased component count. Filters and switches will be combined into one integrated circuit that could eventually be combined with other circuitry such as amplifiers and mixers. The improved frequency selectivity of the switchable narrowband filtering greatly relaxes the dynamic range and power requirements for each stage that follows the filtering, improving both sensitivity and jam resistance. The size, power, component count, and performance improvements will impact a wide range of national-security-related RF systems. With two to four years of technology maturation, this technology will be ready for insertion into systems.

Mesoscale Highly Elastic Structures (MESHES) for Surety Mechanisms
141689

Year 2 of 3
Principal Investigator: B. H. Jared

Project Purpose:
The purpose of this project is to investigate a new approach to mesoscale elastic elements that meet advanced requirements for surety mechanisms. Current coil-wound wire springs have high variability due to material and process variations forcing mechanism parts to be significantly overdesigned, antithetical to design goals requiring reduced mass and improved response time. Mesoscale highly elastic structures (MESHES) will be demonstrated that yield repeatable spring response with lower component uncertainties. Required research includes investigations of material science and direct machining processes at the mesoscale and the ability to accurately predict performance of complex, 3D, highly elastic structures including material response and surface effects from the fabrication processes. Important research will include the material properties of small features where assumptions of homogeneity break down. This breakdown is especially important for highly elastic members but will apply to small features in weapons components and to small mechanisms in general. Process research will quantify the surface effects of several machining processes and evaluate their modification of material behavior in mesoscale structures. Design development will integrate material and process understanding into an integrated design capability, including strategies for creating spring-like response from fundamentally different structures. The resulting structures will exhibit significantly higher repeatability than wire-wound springs and will significantly open the design space to new materials, new geometry, and added capabilities. The results will be applicable to all surety mechanisms and will also have application to small mechanisms in general.

Summary of Accomplishments:
Steady project progress continues as FY 2011 efforts have focused on the design, fabrication, and testing of prototype MESHES springs. Design efforts have used two different baseline extension springs. Initial MESHES equivalent springs were designed based on a single start, 3D coil geometry produced from 304L hypodermic needle tubing. After design optimization, initial prototypes were fabricated. Recent springs have been produced in collaboration with external vendors, anticipating a need for larger spring quantities in testing and for gaining insights on potential production margins. Process improvements have been observed with each part set (both internal and external), as recent springs have shown measured stiffness variations of only 10% and agreement with model predictions to within 5%. An equivalent planar geometry has been designed that will facilitate the use of materials with varying thickness and grain structure to better understand the anticipated limits of continuum assumptions in spring models. Preliminary fatigue tests have also proven successful with as-machined springs demonstrating fatigue life from 10^3-10^6 cycles, dependent on loading conditions. An order of magnitude improvement in fatigue life has also been observed with the introduction of a post-machining electropolishing step. Optimal removal rates and surface modifications in 304L hypodermic needle tubing have been determined using a matrix of process parameters for varying aspect ratios and initial surface finishes.

Significance:
Sandia's primary mission to maintain nuclear weapons (NW) surety in the face of evolving threats requires continued development of sophisticated surety strategies. Many of these strategies require decreases in volume and mass of mechanisms to add capability within space constraints and to enable shortened operation times. A further constraint to these strategies is the continual desire for improving mechanism quantification of margin and uncertainty (QMU) either through improved design or reduced

process uncertainties. MESHES will address each of these fundamental needs through the development of smaller highly elastic structures with improved reliability, uncertainty, and performance that will support arming, fuzing, and firing (AF&F) developments, a core Sandia product.

Selective Stress-Based Microcantilever Sensors for Enhanced Surveillance
141691

Year 2 of 3
Principal Investigator: M. D. Allendorf

Project Purpose:
Assessment of component aging and degradation in weapon systems remains a considerable challenge for the Integrated Stockpile Evaluation Program. Analysis of weapon atmospheres can provide degradation signatures and indicate the presence of corrosive vapors. However, a critical need exists for compatible in-situ sensors to detect moisture and other gases over stockpile lifetimes. This inhibits development of both "self-aware weapons" and fully instrumented weapon test platforms that could provide in-situ data to validate high-fidelity models for gases within weapons. We will develop a platform for on-demand weapon atmosphere surveillance based on static microcantilevers (SMC) coated with nanoporous metal organic frameworks (MOFs) to provide selectivity. SMC detect analytes via adsorbate-induced stress and are up to 100x more sensitive than resonant beam designs. They are also low-power, highly compact devices that can be manufactured using complementary metal oxide semiconductor (CMOS) technologies. MOFs have ultrahigh surface areas (up to 6000 m^2/g), are extremely radiation resistant, and have a hybrid inorganic-organic structure providing much more flexibility to tailor pores for selective adsorption than any other nanoporous material. We will create MOF-based recognition chemistries for H_2O, CH_4, O_2, and other gases using validated atomistic modeling tools to guide synthesis. A stress-based hydrogen detection capability using a NiPd coating will also be tested. MOFs exhibiting large adsorbate-induced structural deformations will be used to maximize sensitivity by creating large interfacial stresses. Novel cantilever designs incorporating reference cantilevers and integrated temperature measurement for in-situ self-calibration will be fabricated. Sensors operating in either dosimeter or real-time mode will be developed. Finally, using simulated weapon atmospheres, long-term device performance (drift, calibration, noise, and cross sensitivity) will be quantified. The project leverages the Center for Integrated Nanotechnologies (CINT) microcantilever discovery platform, Microsystems and Engineering Sciences Applications (MESA), and an ongoing collaboration with Georgia Tech School of Mechanical Engineering to develop static microcantilevers (SMC) devices, fabrication methods, and data collection strategies.

Summary of Accomplishments:
A detailed investigation of the layer-by-layer (LBL) growth process for CuBTC, the Metal-Organic Framework (MOF) selected for humidity detection, was performed, including assessment of the effects of temperature, concentration, and substrate on the growth rate. Crystallinity, roughness, and adhesion were also characterized. From this investigation, we determined optimal processing conditions for CuBTC growth. We also explored alternative methods to LBL growth and tested them with promising MOFs for methane detection; films of the MOF DUT-6 were successfully grown. Atomistic modeling was performed to identify promising MOFs for CH_4 and O_2 detection. Linker functional groups and other pore attributes were evaluated to determine which have the greatest effect on CH_4 uptake, including amine functional groups, solvent, and pore size. Results suggest detection of 5 ppm CH_4 is feasible with a microcantilever. Moisture detection using CuBTC-coated surface acoustic wave (SAWS) was fully characterized over the –70 to 10 °C frost point range; a provisional patent application was submitted. The H_2O sensors were evaluated for cross sensitivity to CH_4 and O_2 and are blind to these gases. The optimal CuBTC thickness for maximum response was determined. A systematic analysis of the effects on microcantilever detection sensitivity of MOF mechanical properties, film thickness, density, and composition of the microcantilever beam was performed. We find that the use of silicon dioxide over silicon nitride as a support structure in the cantilever increases its response. Among the MOF properties, Young's modulus and Poisson's ratio have the greatest effect on the cantilever

response, while the effect of MOF density is negligible. A testing protocol was developed to provide benchmark properties for each microcantilever sensor prior to and after MOF coating. A microcantilever fabrication run was completed at Georgia Tech, yielding three wafers with ~80 functioning sensors. Three journal articles, one book chapter, and five conference presentations (two invited) were completed.

Significance:
A state-of-health predictive capability is a critical aspect of the Integrated Stockpile Evaluation (ISE) embedded-evaluation contribution to Common-Adaptable-System-Architecture (CASA) stockpile transformation objectives. A second key application is deployment in the emerging ISE component surveillance program (CSP). DOD has analogous needs: a prognostic health monitoring system is required in all new major systems. A third application is for DHS-related real-time chemical detection schemes.

Refereed Communications:
T. Zeitler, M.D. Allendorf, and J.A. Greathouse, “Grand Canonical Monte Carlo Simulation of Low-Pressure Methane Adsorption in Nanoporous Framework Materials for Sensing Applications,” to be published in the *Journal of Physical Chemistry C*.

M.D. Allendorf, A. Schwartzberg, V. Stavila, and A.A. Talin, “A Roadmap to Implementing Metal-Organic Frameworks in Electronic Devices: Challenges and Critical Directions,” *Chemistry*, vol. 17, pp. 11372-11388, October 2011.

L.E. Krenoa, K. Leong, O.K. Farha, M.D, Allendorf, R.P. Van Duyne, and J. T. Hupp, “Metal-Organic Framework Materials as Chemical Sensors,” to be published in *Chemical Review*.

B.W. Jacobs, R.J.T. Houk, B.M. Wong, A.A. Talin, and M.D. Allendorf, “Electron Beam Synthesis of Metal and Semiconductor Nanoparticles Using Metal-Organic Frameworks as Ordered Precursors,” *Nanotechnology*, vol. 22, p. 375601, September 2011.

The Role of Hydrogen Isotopes in Deformation and Fracture of Aluminum Alloys
141692

Year 2 of 3
Principal Investigator: C. W. San Marchi

Project Purpose:
Tritium reservoirs for Gas Transfer Systems are high-energy-rate forged austenitic stainless steel. The forging process is designed to control strength, grain size, dislocation microstructure, and forging flow lines. Commercial operations do not attempt to simultaneously satisfy all of these materials variables in forged product, making it difficult to source forgings from the commercial sector. Aluminum alloys represent a potential alternative to forged stainless steel for tritium containment with several important advantages. Structural aluminum alloys can be strengthened by precipitation, eliminating the need for forging. In addition, aluminum alloys have very low solubility of hydrogen, which may explain the perception that they are "immune" to gaseous hydrogen. Due in part to the difficulties of observing hydrogen in metals and executing tests in high-pressure gaseous hydrogen, the scientific foundation for establishing immunity of aluminum to hydrogen-assisted fracture has not been adequately demonstrated in the literature. Hydrogen transport within the metal must precede hydrogen-assisted fracture, and this limiting condition appears impossible to quantify in conventional testing. This project seeks to clarify the surface kinetics of hydrogen uptake and transport in aluminum alloys during exposure to gaseous hydrogen and to determine the structural compatibility of aluminum in high-pressure gaseous hydrogen. We plan to employ advanced characterization techniques to enhance the understanding of the thermodynamics and kinetics of both hydrogen on the surfaces of aluminum alloys and hydrogen transport in the bulk. Knowledge of this physics will be coupled with testing in the high-pressure hydrogen laboratory with the aim of establishing methods for determining conservative engineering properties appropriate for the design of aluminum vessels for the containment of high-pressure gaseous hydrogen and hydrogen isotopes. Unique facilities exist at Sandia, which are necessary to illuminate the fundamental physics of hydrogen-aluminum interactions (including low energy ion scattering and thermal desorption spectroscopy, as well as mechanical testing in gaseous hydrogen at pressure up to 138 MPa).

Summary of Accomplishments:
Surface studies have produced real-space scattering maps of the aluminum surface, and modeling tools have been developed to simulate the experimental results (Kolasinski, et al., *Nucl Instrum Meth B*; doi:10.1016/j.nimb.2010.11.038). Adsorption-desorption kinetics of hydrogen on aluminum has also been examined. Capability for Auger electron spectroscopy has been added to equipment to identify the role of oxygen on these measurements, greatly enhancing the uniqueness of the Angle-Resolved Ion Energy Spectrometer (ARIES). These results provide the groundwork for identifying the binding sites of hydrogen on pure aluminum and aluminum alloys.

Thermal exposure and deuterium aging studies have shown that hydrogen can be removed from aluminum alloys and be replaced with deuterium. More work is necessary to optimize treatments for controlling hydrogen-deuterium concentrations from gas-phase exposure. Thermal desorption experiments have shown that trapping of hydrogen in aluminum alloys is dependent on composition and/or structure. In pure aluminum, measured trap energies are being linked to microstructural features, which may provide insights into the effects of hydrogen on deformation and fracture. Of particular interest to mechanical testing, hydrogen uptake is not dependent on surface condition in hydrogen permeation experiments, implying that testing is not limited by surface kinetics. Work is continuing on quantifying hydrogen trapping in engineering alloys.

Fracture tests on aluminum alloys have not revealed any measurable effect of high-pressure gaseous (dry) hydrogen on several aluminum alloys. Fatigue crack growth tests were implemented since these tests can expose freshly crack surfaces to hydrogen environments for significantly longer time periods than the monotonic loading of fracture tests. These fatigue tests appear to be the first reported high-pressure fatigue tests on aluminum alloys (San Marchi, et al., ASME PVP-2011 Conference paper no. PVP2011-57701). Additional fracture and fatigue tests are planned to verify the initial trends and demonstrate broad applicability.

Significance:
To enhance reliability and expand design space, new structural materials must be identified for tritium compatibility in nuclear weapons applications; aluminum is the obvious candidate for improving manufacturability and long-term reliability for tritium service. As this work uses hydrogen as a surrogate for tritium, the results obtained in this study have broad applicability to the containment of gaseous hydrogen, as in hydrogen fuel cell systems. In particular, aluminum is an important structural material in the context of establishing energy security; aluminum represents a desirable alternative to the expensive materials currently in use for engineering systems using hydrogen as an energy carrier. This work may provide some initial technical basis for the use of aluminum in gaseous hydrogen systems, thus lowering barriers to market penetration for hydrogen-energy technologies.

Trusted Computing Solution for an Untrusted Computing Environment
141700

Year 2 of 3
Principal Investigator: W. R. Johnson

Project Purpose:
Sandia's DOE, NNSA, and other government agency programs necessarily rely on commercial off-the-shelf (COTS) computing platforms (including hardware and software) to process, store, and share mission-critical, product-related information. Rootkits are an emerging class of malware (malicious software) that target COTS computing platforms at lower layers in the hardware/software stack and, as a result, have proven to be relatively immune to the defenses of anti-virus software. Various techniques have been employed at the hardware level in an attempt to defend against this class of malware with very limited success. The concept of a hardware/software trust anchor (developed at Sandia) leverages the best features of these attempts, and early development has shown a great deal of promise in its ability to solve this extremely difficult problem.

We are developing a reusable trusted computing platform designed with security in mind in order to meet the needs of a trust-anchor solution, thereby providing the means to protect critical program networks. Commercial processors are more than capable of providing the processing and communication needs of a trusted hardware platform, but due to their complex nature and performance driven design, do not lend themselves to analysis and validation of reliably secure execution. The absence of commercially viable options drives the need for development of a computing resource designed with trust and security in mind (not performance). The capabilities of this trusted computing solution are synergistic with the needs of many other product areas and, therefore, have direct application in these areas as well.

Summary of Accomplishments:
The topic area of Trusted Computing was analyzed and a first-order Trusted Computing Taxonomy was designed and described. The taxonomy was in response to differing experiences, views, and terminology when describing trust and trusted computing. Sandia has unique and mission centric resources in this area, and the taxonomy benefited from these resources through the understanding that trust, notional or formal, must be designed in the appropriate locations of the greater systems context. Sandia has a rich set of trusted designs that gain trust by constraining the greater application context in ways that can be enumerated and examined.

The Trusted Computing Taxonomy (TCT) dovetails with the notion of constraints and constraint-based systems by systematically reducing and/or simplifying the problem space of a trusted application. This methodology can have application in the area of formal analysis if the system and its trust components, processes, and architecture are appropriately analyzed.

Significance:
Analysis of existing trusted systems within the national security mission at Sandia shows that, while trust is well warranted in the applications deployed on the trusted systems, it is not always clear that the architectural implementation is trustworthy. Trust is ultimately placed on/in the design architects and support team as they are able to explain on a case-by-case basis how the trusted system will operate when an attempt to compromise nominal functionality occurs. The downfall here is that it is increasingly difficult to understand how the system works and how it may be affected by life-cycle modification or adversary attack.

Using the TCT, it becomes possible to normalize system descriptions, functionality areas, and, in the case where a rigorous constraint system is formally applied with the taxonomy, assertions on cause and effect can be made on system alterations and malicious attack without brute force analysis with peer review.

Localized Temperature Stable Dielectrics for Low Temperature Co-Fired Ceramic
148900

Year 2 of 3
Principal Investigator: S. X. Dai

Project Purpose:
Low-temperature co-fired ceramic (LTCC) is a multilayer 3D packaging, interconnection, and integration technology. In the past 10-15 years, the biggest growth of LTCC technology occurred in wireless communications ranging from radio frequency (RF) to microwave (MW) frequencies. The three key material parameters most important to this application space include dielectric constant ε, quality factor Q (inverse of dielectric loss), and temperature coefficient of resonant frequency, T_f. For RF/MW circuits incorporating resonator functions, it is highly desirable to have a zero or near-zero T_f ($0T_f$) to fully utilize the communication bandwidth and achieve temperature stability of devices. However, all current commercial LTCC systems have a T_f in the range –50 ~ -80 ppm/ °C. There were several successful attempts to formulate $0T_f$ LTCC base dielectrics, but so far the efforts to develop $0T_f$ LTCC system, including conductors and other embedded materials that are compatible with $0T_f$ base LTCC dielectric, have not been successful.

Instead of developing an entirely new $0T_f$ LTCC system, our approach is to establish localized $0T_f$ structure in most widely used LTCC systems to take advantage of existing LTCC technologies and infrastructure. We will explore a method to achieve $0T_f$ by: 1) developing novel compensating materials which have opposite T_f to that of the LTCC base dielectric, and 2) incorporating the compensating material locally to LTCC structures where the resonant functions reside. The key materials science challenges include synthesis of T_f-compensating materials and tailoring of their compatibility, both physical and chemical, to the existing LTCC system. Our objective is to examine the concept of localized temperature stability for advanced RF/MW applications by addressing related materials science and engineering issues.

Summary of Accomplishments:
T_f compensating materials development:
A series of formulations, 0.55wt% V1449 glass+ xwt% Al_2O_3 + (0.45-x)wt% TiO_2/$CaTiO_2$/$SrTiO_3$, have been formed as T_f-compensating materials. Sintered density as well as dielectric properties of these compositions in pellet form, have been characterized. A composition, STO20 at 0.55wt% V1449 glass+ 25wt% Al_2O_3 + 20wt% $SrTiO_3$ has been down selected as the T_f-compensating materials based on: 1) high sintered density, 2) cofireable with 951 LTCC, and 3) high temperature coefficient of capacitance.

$0T_f$ stripline resonator:
Stripline ring resonators were fabricated in 4-layer DuPont 951 LTCC panels. The T_f of base 951 LTCC is -68.5ppm/ °C. STO20 paste was printed over the resonator Au conductor line for T_f compensation. With a single layer of STO20 on one side of the ring, the T_f decreased to ~ –33 ppm/ °C. For a double layer STO on both sides of the ring, the T_f approached 0ppm/ °C. The initial results demonstrated the feasibility of localized temperature compensation to realized $0T_f$ in a multilayer LTCC package.

Invention disclosure and presentation:
An invention disclosure has been submitted. Patent filing is scheduled for October 2011. The initial results will be presented at the IMAPS2011 conference in October 2011. A manuscript has also been submitted to the conference proceeding.

Looking forward:
Additional STO compositions have been formulated to explore the composition window of the T_f-compensating materials. Different configurations of STO layer placement in the resonator panels will be tested to study the effect on T_f compensation. Electromagnetic simulation and modeling using dielectric composite theorem will be conducted to validate the experimental results.

Significance:
Localized $0T_f$ dielectric provides a unique technical solution for advanced radio and microwave frequency circuitry. Devices utilizing this technology correspondingly provide inherent temperature stability. This proposed effort addresses a key technology need for highly temperature stable modules in nuclear weapons systems as well as radar applications for homeland security. The research fits well into DOE's mission in terms of nuclear security and scientific discovery and innovation.

Development of Ab-Initio Techniques Critical for Future Science-Based Explosives R&D
151351

Year 1 of 3
Principal Investigator: R. R. Wixom

Project Purpose:
Density Functional Theory (DFT) has emerged as an indispensable tool in materials research, since it can accurately predict properties of a wide variety of materials at both equilibrium and extreme conditions. However, for organic molecular crystal explosives, successful application of DFT has largely failed due to the inability of current exchange-correlation functionals to correctly describe intermolecular van der Waals' (vdWs) forces. Intermolecular vdWs forces are critical to predicting the chemistry and physics of explosives at both equilibrium and under stimuli. For the explosive pentaerythritol tetranitrate (PETN), vdWs interactions dominate the physics for isotropic pressures up to 10 GPa, which implies that we cannot accurately apply DFT for investigating aging, safety, or the margins associated with initiation of PETN or any high explosive. This is unfortunate since explosives research is extremely difficult, expensive, and dangerous, while at the same time essential to DOE/NNSA core missions.

We propose to construct a completely new functional using the subsystem functional scheme that was recently used to successfully include correct surface treatment into the AM05 functional (published by Armiento and Mattsson, 2005). Despite decades of research, resulting in hundreds of approximate functionals, no functional treating of both vdWs and stronger bonds with equal accuracy is available. Even though the vdWs problem can be circumvented by performing DFT-AM05 calculations only at very high pressure, successful investigations at equilibrium and low compression (weak shock), where vdWs forces dominate, will require a new functional provided by a more sophisticated approach such as the subsystem functional scheme. This new functional will provide an accurate first-principles link to the ongoing mesoscale and continuum physics efforts to model explosive components, and additionally will have broad, dramatic impact across many fields of science including energy, biology, pharmaceuticals, and the study of any weakly bonded materials systems, such as polymers and those applications involving graphene.

Summary of Accomplishments:
We have identified a model system that we believe represents the physics present in van der Waals' bonding. The model we are using comprises two parallel plates with charge-filled vacuum between them. A many-body Hamiltonian for carriers in the region between the plates has been written, and we are still working towards finding the ground state solution, which is not a trivial effort. It is expected that the solution to this problem will have broad impact beyond the study of van der Waal's bonding.

We have also made significant progress in collecting and generating materials data needed for validation. For two materials, PETN and hexanitrostilbene (HNS), we have performed an extensive set of calculations. From those calculations, we have obtained first-principles generated shock Hugoniot data, which has been valuable in understanding the nature of the intermolecular bonding in these materials but has also provided more accurate equations of state (EOS) for use in hydrocode simulations. Preliminary EOS models have been generated for these materials and are currently being tested for their predicative capabilities. We have presented this work at two high-profile shock/explosives conferences, first at the EuroPyro 2011 in Reims, France and then at the American Physical Society (APS) meeting on Shock Compression in Condensed Materials. A paper was also published in the proceedings of the EuroPyro meeting, and several journal articles are in preparation.

We have built and demonstrated a diamond-anvil-cell system for performing high-pressure isothermal compression experiments on explosives. This capability had previously been lost, but is now revitalized and will benefit Sandia's energetic materials research community.

Significance:
DFT calculations are invaluable in many fields of science, elucidating difficult and important problems ranging from fundamental physics/chemistry to applied materials science. However, many DOE strategic themes involve materials problems where DFT has yet been unable to fully contribute; many key problems in energy, biology, environment, and nuclear weapons involve physics dominated by weakly bonded materials. Development of a functional that is accurate for both weakly and strongly bound systems is the critical next step if DFT is to play a role in the crosscutting science integration facilitating transformation of the nuclear weapons complex and enabling broad ranging technologies for nuclear security.

Metal-Insulator Transition-Based Limiters
151352

Year 1 of 3
Principal Investigator: C. Nordquist

Project Purpose:
Limiters are essential for protecting receivers in radars, as they provide protection by passing low-level signals but blocking high-power signals that could damage sensitive electronics. Novel materials and devices provide potential for improved bandwidth, insertion loss, and power handling. Existing limiters, using semiconductor diodes, are generally restricted by capacitance that forces undesirable compromises among bandwidth, power handling, sensitivity, and survivability. Metal-insulator transition (MIT) materials offer the potential for revolutionary improvement of radio frequency (RF) limiters. Recently, promising microwave power limiting was reported using vanadium dioxide, a material exhibiting a thousand-fold change in resistance at a specific transition temperature. Microwave heating at high power can trigger this MIT and create a reversible short circuit, reflecting undesired energy away from the receiver. Because the limiting mechanism is purely resistive, these materials may enable broadband, low-loss, high-power limiters with a small footprint when compared with conventional limiters. We are investigating reversible MIT materials for improved radar systems and applying these materials to prototype demonstration devices. We are investigating material fundamentals with a goal of tailoring the transition temperature, increasing the resistance ratio, and developing integration approaches. A device thrust motivates the materials requirements, applies the materials to demonstrate RF limiters, tests the limiters under continuous and pulsed RF power, and provides feedback for further materials development.

This research is appropriate for LDRD because MIT RF devices are currently at TRL2, with only one demonstration of functionality (aside from this work) reported to date. No reports of parameters critical to pulsed radar operation exist, with unknowns including power handling, transient behavior, and recovery time. These unknowns regarding the materials integration and device performance make this effort too immature for direct funding. If this project is successful, it will establish a technology foundation that will improve the survivability of radar systems.

Summary of Accomplishments:
In the first year, we have developed a method of depositing and creating vanadium dioxide films (VO_2) on both silicon and glass, with the films demonstrating transition temperatures at the expected 68 ˚C and resistance ratios up to 1000. To rapidly characterize these films, we developed a four-point-probe station with automated resistance measurement over temperature ranges from ï 50 ˚C to +200 ˚C and have characterized several dozen films. A combination of optical, x-ray, spectroscopic, and electrical characterization has allowed us to identify the properties of this material in compositions ranging from oxygen-poor to oxygen-rich. Additional measurements under way at partner universities are beginning to reveal the mechanism of electrical transport.

In addition to the VO_2 films, we have also characterized two chalcogenide films, with transition temperatures exceeding 180 ˚C. However, achieving a reversible conductivity transition with these films has not been demonstrated, restricting their usefulness in a limiter. We will continue to explore this class of materials because of their high transition temperature and high contrast ratio. Additionally, these materials hold promise for other types of reconfigurable integrated circuits. We have demonstrated circuits with VO_2 films integrated into a microwave integrated circuit technology, including 200 ohm/square TaN resistors, SiN metal-insulator-metal capacitors, and transmission lines. Using this process, we have demonstrated shunt limiter elements with <2 dB of insertion loss and >35 dB of isolation from DC to beyond 5 GHz and limiters capable of holding off >20 W of continuous power at 1.7 GHz. We have begun pulsed measurement, and expect to continue improving the contrast ratio of the limiter material and increasing the transition temperature of the limiters in the next year.

Significance:
By performing science-based materials development, this project supports DOE's scientific discovery and innovation mission. By impacting the size and performance of future radar systems, the project will support the DOE strategic theme in nuclear security and deterrence. Additionally, an innovative RF technology solution will appeal to other agencies and external partners that are interested in novel RF electronics.

The development and integration of this new materials capability can also be applied in areas outside of the limiter, such as for reconfigurable RF integrated circuits, thermal and energy detection, and energy conservation initiatives such as smart windows.

Additionally, the materials and device work being performed is suitable for publication in peer-reviewed journals and publication at technical conferences, providing publicity for Sandia.

Thermoelectric Materials: Mechanistic Basis for Predictive Aging Models and Materials Design
151353

Year 1 of 3
Principal Investigator: D. L. Medlin

Project Purpose:
New thermoelectric devices are being developed for use as long-lived power sources for the nuclear stockpile. These devices rely on thermoelectric materials, based on alloys of Bi_2Te_3, to perform the active function of converting heat flow to electrical power. Regardless of the final design and the specific heat source, the long-term performance of these devices ultimately rests on the long-term properties of the thermoelectric materials. Understanding the aging mechanisms of the relevant Bi_2Te_3-based materials (including changes in the material and its interaction with contact materials) is critical if we are to confidently predict and support the 15-30 year performance of these devices. Looking forward, we also recognize that advances in nanoscience and control of electronic structure are yielding unprecedented improvements in thermoelectric materials technology — advances that are now extending to bulk Bi_2Te_3-based materials in the temperature ranges relevant for stockpile application. A fundamental understanding of the interplay between performance and stability will be critical in developing new materials that take advantage of these recent advances while maintaining the reliability required for adoption into the future stockpile.

To provide this understanding, we propose a comprehensive program of experiment and materials theory and modeling. Our goal is to discover and quantify the mechanisms governing the performance and long-term behavior of Bi_2Te_3-based thermoelectric materials and to integrate these findings into a predictive science framework. To reach this goal, we will draw on advanced tools for microscopy and transport analysis, and we will advance the state-of-the-art in modeling both materials stability and thermoelectric properties. This capability and knowledge base will be important in future years in meeting our long-term responsibility for the new Bi_2Te_3-based thermoelectric power systems currently being developed for the stockpile and in guiding the engineering of more advanced thermoelectric materials for improved reliability and tailored thermal response specific to stockpile-application needs.

Summary of Accomplishments:
We have conducted annealing experiments to investigate the diffusion of contact material into the bulk thermoelectric element. We have investigated the interaction of gold, a candidate contact material, with commercial n-type bismuth telluride ($Bi_2(Se_{1-x}Te_x)_3$). Our measurements using secondary ion mass spectrometry (SIMS) confirm rapid diffusion of low levels of Au even at low temperatures.

We are also measuring the time dependent variation of the Seebeck coefficient and electric conductivity. Our initial measurements on commercial n-type Bi_2Te_3 have shown changes in the electronic transport properties, including reduction in the electric resistivity and a reduction in the magnitude of the Seebeck coefficient at low temperatures. A likely mechanism for these changes, which we will explore in our upcoming work, is loss of tellurium. We have also initiated time-dependent measurements to monitor the variation of transport properties with the Au contact materials.

We have fabricated Bi_2Te_3 material of well-understood microstructure and processing conditions, which can be compared against the behavior of commercial device grade material. Based on our review of the literature, we have chosen extrusion as a method to suitably tailor an anisotropic crystallographic texture. Our diffraction measurements have confirmed an appropriate crystal texture in this material. We have also initiated transmission-electron-microscopic studies of these materials to clarify the interface and defect structures.

Finally, we are also developing the theoretical frameworks required to model the aging mechanisms and thermoelectric transport properties in Bi_2Te_3. We have performed preliminary diffusion simulations of contact metal into single crystal and polycrystalline Bi_2Te_3 using Sandia's Aria coupled multiphysics code, taking into account anisotropic diffusivity. We are working with the Aria development team to implement a Soret term for the diffusive flux. In parallel, we have also conducted density functional theory calculations to investigate the changes in electron structure that occur at embedded interfaces in Bi_2Te_3.

Significance:
This work is directly relevant to ongoing development of long-lived thermoelectric power sources for the nuclear stockpile. More broadly, thermoelectrics have applications for DOE energy missions (e.g., waste-heat recovery for energy efficiency) and DOD and DHS national security missions (e.g., cooling for improved detector performance).

Refereed Communications:
P.A. Sharma, A.L. Lima Sharma, D.L. Medlin, A.M. Morales, N. Yang, M. Barney, J. He, F. Drymiotis, J. Turner, and T.M. Tritt, "Low Phonon Thermal Conductivity of Layered $(Bi_2)_m$-$(Bi_2Te_3)_n$ Thermoelectric Alloys," *Physical Review B*, vol. 83, p. 235209, 2011.

Software-Defined Telemetry Using Programmable Fuzing Radar
151354

Year 1 of 3
Principal Investigator: D. Young

Project Purpose:
Recent advances in technology have led to the availability of high-speed digital-to-analog converters (DAC), wideband quadrature modulators, and signal processors with great computation capability. The purpose of this project is to develop and demonstrate the combination of radar and telemetry functionality into a single piece of hardware.

Combining both functions into the same war-reserve hardware has the potential of reducing the cost and, more importantly, improving the fidelity of telemetry-instrumented flight tests. Fewer modifications to the electronics and physical structure of the weapon should increase the potential for revealing critical issues.

A number of interesting technical issues will need to be resolved to realize the promise of radar-integrated telemetry. Power, modulation, and transmit times need to be optimized so that telemetry and radar operate simultaneously. Novel hardware arrangements will be constructed to provide multiple functionalities, and signal-processing algorithms will be developed to mitigate interference.

Summary of Accomplishments:
The team has considered multiple hardware architectures and decided on a direct synthesis and direct sampling architecture. The design for prototype hardware is finished and fabrication of the first prototypes is nearly complete, ahead of schedule. We expect to perform a basic loop test (where the radar transmits and receives a test signal) using the new hardware early next fiscal year. Continuous wave and pulsed radar designs using direct sampling have been designed and simulated in Simulink. Incorporation of telemetry signaling and adaptive filtering is in progress. Some simulation work remains to be done in the next fiscal year.

Significance:
Significant cost savings could be achieved by combining the radar and telemetry transmitter. Sandia would no longer need to rely on commercial companies to provide the telemetry transmitter and would not be subject to the high costs incurred when switching vendors. Integrating the radar and telemetry transmitter would also increase the fidelity of tests — fewer changes to the weapon would be required for instrumented flight tests. Fewer modifications mean that results from tests are more likely to reveal real problems.

More immediately, the prototype hardware is of current interest to Sandia's synthetic aperture radar (SAR) community because of its wide bandwidth.

Non-Destructive Gas Pressure Measurements in Neutron Tubes and Generators
151355

Year 1 of 3
Principal Investigator: R. S. Goeke

Project Purpose:
Neutron generators are a key limited-life component in nuclear weapons and other applications requiring a neutron source to probe or activate a material for analysis. At the heart of the neutron generator is a high-voltage vacuum tube which contains tritium hydride. Measuring the pressure inside the tube is a difficult proposition that typically requires destructive analysis. An accurate measurement of the pressure over a large range of vacuum is desirable but has not been possible. We plan to solve this challenge by treating the existing vacuum envelope as a Penning or Redhead style ion gauge. By creating optimized cross-electrical and external magnetic fields on the existing tube design, we can enhance the electron ionization path and generate a measureable signal into the high vacuum regime. This capability can be applied to any vacuum tubes with two or more electrodes.

While the concept of treating a neutron tube or switch tube as an ion gauge sounds simple, the materials, geometry, and small volumes have prevented previous attempts to measure high vacuum levels. We hope to overcome this by modeling and optimizing the fields for our test system. Characterization of emission fields and ionization thresholds for existing tube geometries should allow us to succeed when this wasn't previously possible.

Summary of Accomplishments:
During the first year, we created a model which demonstrated the feasibility for creating a self-sustained Townsend discharge between two electrodes in vacuum using crossed electric and magnetic fields. The computer model was created using the physics simulation code Aleph, developed by Sandia's Advanced Simulation and Computing (ASC) Program. The Aleph model established the conditions required to trap electrons in crossed fields with enough energy to ionize gas molecules. The magnetic fields from an existing 2" magnetron, which was removed from a sputter cathode, was profiled with a gauss meter and used as the base design for the magnetic fields.

To validate this model, a vacuum test stand has been designed and fabricated. This high-vacuum system has multiple high-voltage feedthroughs, which enable charging electrodes to 20kV and the measurement of electron currents down to 1 pico-amp. The system is pumped by a turbo-molecular pump and reaches base pressures of 1×10^{-8} torr. Also included is the capability to introduce gases such as helium at fixed flow rates, which will allow testing over a controlled range of pressures.

Initial testing has begun using simplified electrode geometries which consists of a 0.5" metal sphere and a 1.5" flat metal disk. These simplified electrodes are being used to validate the computer model before moving to classified geometries. The flat disk electrode presently sits on the 2" magnetron and works as the gauge cathode.

Our initial testing has demonstrated that a Townsend discharge can be initiated with this configuration. At a sphere to disk spacing of 0.5", an 800 gauss field at the disk surface, and +2kV on the sphere, a sustaining discharge strikes with a measurable pressure-varying current starting at a pressure of 10^{-5} torr. These conditions and results are preliminary but demonstrate the validity of this research approach.

Significance:
Sandia has responsibility for neutron generators used in the US nuclear stockpile from design to end of life (EOL). The poor vacuum in the tube can result in failure. Currently, it is difficult, expensive, and time consuming to measure the vacuum level of a neutron tube. This proposal will develop a fast, inexpensive, and non-destructive technique to determine the vacuum quality inside any neutron tube/generator to allow an accurate determination of the tube's vacuum state-of-health. This information will rapidly provide assurance of the neutron generator's performance with no destructive testing.

All-Optical Fiber Architecture for Direct Optical Ignition
151356

Year 1 of 3
Principal Investigator: S. E. Bisson

Project Purpose:
Direct optical ignition (DOI) has long been recognized as an attractive alternative to conventional explosives initiation techniques, offering enhanced safety from unintended initiation by external electrical and/or optical energy sources. Current DOI concepts are based on traditional Q-switched bulk solid-state lasers, comprising a bulk optical resonator and numerous other bulk optical components for Q-switching, power splitting, and fiber coupling. While significant progress has been made with this particular approach, complexity is — in general — high, size is also an issue, and alignment sensitivity can be a serious problem. While the detailed requirements may vary depending on the particular device, attributes such as compact size, low weight, low power consumption, and susceptibility to high-g loads are common requirements. To meet these challenging requirements, we propose a radically new design for DOI based on a highly integrated, distributed passively Q-switched, pulsed fiber light source. This architecture has many potential advantages such as size, simplicity (few components), and alignment insensitivity to shock and high-g environments. This work will focus primarily on technical issues related to the passive distributed Q-switch architecture and is aimed at long-term stockpile needs such as Reentry Vehicles (RVs) and Reentry Bodies (RBs).

Summary of Accomplishments:
The goal of this work was to develop a novel, all fiber approach for optical initiation that could have a broad impact on future stockpile needs. We have now completed our first year of this project and have made significant progress towards that goal. While the application of optical initiation offers many advantages, there are many rigorous requirements that must be met in order to be useful for future stockpile needs. To meet these challenges, we have developed and conducted preliminary testing on an all-fiber architecture that is completely integrated, compact, and robust over a wide range of environments. During the first part of the project, a conceptual design was developed that was compatible with first-order requirements for size, pulse energy, and time-to-fire. Although the number of components was small (approximately five coupled fiber devices), the parameter space was quite large. To optimize the design and minimize the parameter space, a comprehensive physics-based model was developed to elucidate basic fiber laser operation. The model was then benchmarked against results from the literature and against a preliminary design that was tested in our laboratory. Once the model was validated, it was reconfigured as a simulator which allowed physical parameters such as gain length, saturable absorber length, doping concentration, mode ratios, etc., to be varied against each other with constraints on time-to-fire and energy. Results from this study were recently published in a Sandia Report and a peer reviewed journal, *Optics Letters*.

At present, we are using the simulator results to optimize a laboratory design for energy and time-to-fire.

Significance:
This work addresses an important national security need. If successful, it would eliminate the intrinsic vulnerability of existing systems to unintended coupling to external energy sources. The proposed system architecture is both physically robust and suitable for integration with existing hardware. There is considerable technical risk; such a light-source architecture has never been demonstrated before. But if successful, the proposed approach provides a path to finally realizing the benefits of DOI. Successful demonstration of the proposed light source architecture may also provide new research avenues and opportunities for additional applications.

Refereed Communications:

D.B.S. Soh, S.E. Bisson, B.D. Patterson, and S.W. Moore, "High-Power All-Fiber Passively Q-Switched Laser Using a Doped Fiber as a Saturable Absorber: Numerical Simulations," *Optics Letters*, vol. 36, pp. 2536-2538, July 2011.

MEMS Photoacoustic Spectroscopy
151357

Year 1 of 3
Principal Investigator: A. Robinson

Project Purpose:
After years in the field, materials in weapons suffer degradation, off-gassing, and chemical changes leading to build-up of measurable chemical atmospheres. Chemicals can be corrosive to electronics and other materials, causing accelerated degradation and reduced time-to-failure. Even benign compounds may indicate known or unknown age-related issues that require action. Obtaining reliable chemical information from sealed environments is difficult at best. Stand-alone embedded chemical sensors are typically limited in specificity, require electrical lines, and calibration drift makes data reliability questionable. Along with size, these "Achilles heels" have prevented incorporation of gas sensing. Standard optical spectroscopy methods offer a partial solution by keeping most of the analytical hardware outside the weapon. This allows the equipment to be sufficiently complex and sophisticated to perform high-quality measurements and analyses. However, standard hardware and techniques are not directly adaptable for in-situ gas measurements in a weapon. Optical access, sufficient interaction pathlengths, and fiber-optic transmission of useful wavelengths to enclosed areas, including safety exclusion regions, are significant barriers. We are developing a system that successfully addresses these technical issues: all-optical mid-IR (infrared) microelectromechanical systems photoacoustic spectroscopy (MEMS PAS) for safe, in-situ monitoring of weapon environments.

Developing all-optical MEMS PAS presents many challenges and risks and will require several disciplines for success. Combining the required elements of this project has never been performed, as no other application has such rigorous requirements for safety and access to accept the risk associated with this combination of technology integration. Success with this project will create significant advances toward a small yet robust, all-optical method for in-situ characterization of gas composition in war reserve (WR), aging, and shelf life units. This has the potential to enhance reliability of the stockpile through 100% gas surveillance and better understanding of normal gas evolution in the stockpile. Anomaly detection will be possible without adding new sensors. Data will improve quantification of margins and uncertainties.

Summary of Accomplishments:
In the first year, we designed and fabricated two novel light-transduced MEMS acoustic microphones, a light-integrating micro-scale photo-acoustic cell, and an infrared fiber-optic interface. The first MEMS microphone is undergoing characterization, and the second has nearly completed fabrication.

MEMS design was preceded by extensive finite-element mode (ANSYS) modeling of inter-layer and intrinsic stresses, mechanical compliance, dynamic stress on the optical transducers, and optical interactions between light guides and optical resonant cavities. Multiple variations of design parameters were co-fabricated as test matrices to maximize achieving optimal characteristics in the first fabrication run of each main design.

COMSOL, multiphysics software, was used to model acoustic resonances within a conceptual photoacoustic cavity. Results guided construction of a thin and wide non-resonant design. Operation at low kHz frequencies ensures time for molecular relaxation timescales and relaxes constraints on symmetry and acoustic loss mechanisms. A second model simulated the dynamic response of a time-evolving pressure pulse within a vented cavity. This generic model demonstrated coupling of: 1) the heated gas (from light absorption) creating a pressure pulse with conductive losses to the surrounding cavity walls, 2) compressible fluid flow through a small vent to ambient conditions, and 3) structural deflection of the pressure transducer membrane. This model provided insights into the rudimentary workings of the power azimuth spectrum (PAS) micro-cell. Other modeling included transduction of absorbed infrared light into heat and pressure and the wavelength-dependent scattering of infrared light within a gold-coated photo acoustic cell.

Characterization testing began recently after delivery of the first realized microphone design. This novel design transduces motion according to the wavelength of light that evanescently transfers from the main light guide into a resonant one. Test structures show 24% transfer efficiency and a half-maximum peak width of 1.7 nm. Static pressure experiments show linear deflection to the test-range maximum of 2.2 psi.

Significance:

The science and technology under development here will help the US attain its objective of sustaining a safe, secure, and effective nuclear arsenal with a smaller number of weapons. Rich chemical information from reliable embedded sensors will enhance confidence in fielded and stockpiled weapons by verifying the presence of expected degradation signatures and the absence of known or unknown anomalous atmospheres. The capability resulting from this work will help ensure a reliable and responsive nuclear weapons stockpile and will eventually improve DOE's ability to certify the stockpile on an annual basis through 100% surveillance.

New science is being developed as we explore the absorption of light by various chemicals and the resulting dynamic pressurization of micron scale, mechanically compliant cavities. Our novel methods of transducing acoustic deflections into optical signals are highly sensitive and better than commercially available all-electronic devices. Due to the higher sensitivity, radio frequency (RF) immunity, and wireless remote operability, these sensors will find additional applications in atmospheric monitoring, oceanography, and geophysics, to name a few. New science will be published in peer-reviewed journals.

Fail-Safe Feature for Abnormal Thermal Environments Using Shape-Memory Alloys
151358

Year 1 of 3
Principal Investigator: J. R. McElhanon

Project Purpose:
We will increase nuclear safety, security, and performance margins for nuclear weapon Life Extension Programs (LEP) by creating fail-safe devices that are activated by abnormal thermal environments. The proposal describes a revolutionary advancement in nuclear safety architectures through developing high-temperature shape-memory alloys (HTSMAs) as mechanical safeing devices. SMAs are metal alloys that can be mechanically deformed into complex shapes and then, through a solid-phase-transformation, can "remember" the original trained shape upon heating. Commercial SMAs consist of alloys of nickel/titanium (Nitinol) that are application limited due to a maximum phase-transformation-temperature near 100 ˚C, a temperature too low for use in abnormal thermal environments due to overlap with normal environments and production processing temperatures. To create effective mechanical safeing devices, we will develop HTSMAs that have shape transitions at >190 ˚C by alloying nickel/titanium with platinum and other elements. Our approach will operate on the principles of inoperability and incompatibility whereby the HTSMA will: 1) fail irreversibly, 2) fail passively, 3) perform predictably, and 4) operate based on a fundamental "first principle" material response.

This research leverages an emerging materials suite that has recently attracted global attention and represents a research area yet to be developed at Sandia. The work will potentially yield an enormous enhancement in fail-safe device performance. New HTSMAs and prototype devices will be created based on a fundamental, science-based materials investigation in collaboration with National Aeronautics and Space Administration (NASA's) Glenn Research Center (GRC). This work is risky because HTSMAs have not been well characterized or developed into viable devices due to such factors as cost, precision in alloying composition, and incomplete knowledge of alloy transformation properties. A tremendous amount of fundamental research is required to target alloy compositions, properties, and processing techniques that will yield useful abnormal temperature fail-safe devices.

Summary of Accomplishments:
- All milestones are on track for FY 2011.
- Expanded the scope of our work to include fabrication/characterization of HTSMAs to include the ternary compositions TiNiPt, TiNiPd, and TiNiHf:
  - Broadened scope has yielded 12 new HTSMAs.
  - Ternary metal addition provides control over thermomechanical properties.
  - Can access SMA transition temperature (TTs) from sub-ambient to >1000 °C.
- Completed fabrication via arc melting/initial characterization of 30 gram buttons of TiNiPt alloys (13.5–16.5) atomic percent platinum in 0.5 at.% Pt increments). Developed heat treatment capability for homogenization of HTSMAs. Confirmed homogenization by electron probe microanalysis.
  - Alloys have austenite (shape memory) TTs between 24–231 °C.
  - Provided the first fundamental study of the pseudobinary TiNi-TiPt phase.
  - Diagram for $Ti_{50}Ni_{50-x}Pt_x$ alloys in non-linear range.
  - Determined that NiTiPt alloys deviate from linearity in TTs at 13.5 at% Pt.

- Electrical discharge machining (EDM) of piece parts for thermomechanical analysis is under way.
- Developed multiple arc-melting process to ensure alloys are homogeneous on a macroscale.

- Characterized Ti-34Ni-15.5Pt (austenite TT=180-190°C) alloy by DSC, DMA, XRD, and resistivity measurements:
  - 3-point bend shape recovery experiments of this alloy exhibited the two-way shape-memory effect (TWSME). TWSME has never been reported for cast TiNiPt alloys.
  - Evaluating the TWSME as a high temperature two-way shape-memory actuator.
- National Aeronautics and Space Administration (NASA) Glenn Research Center (GRC) completed fabrication of a series of TiNiPd and TiNiHf alloys via vacuum induction melting:
  - Processed 500g melts of Ti-50.3Ni-(22-24)Hf and Ni-50.5Ti-25Pd.
  - Ti-50.3Ni-(22-24)Hf initial thermal TT characterization is under way.
  - Ni-50.5Ti-25Pd initial austenite TTs for two separate ingots are 164-187 °C and 205-228 °C.
- Modeling:
  - Assessed the current SMA-enabled hurricane spring concept to determine model features necessary to satisfy simulation requirements.
  - Identified constitutive models and implementations amenable to the simulation of third-year milestone spring.
- Programmatic Growth/Leveraged Work:
  - Established processing and modeling collaboration with Texas A&M University.
  - Transportation Safeguards and Surety Department collaboration.
  - Collaboration with Los Alamos National Laboratory.
  - Delivered HTSMA fail-safe prototypes to customer.
  - LDRD progress presented at the Joint Working Group (JOWOG) 28 June 2011.

Significance:
FY 2011 work has resulted in developing a fundamental understanding of the effects of alloying platinum, palladium, and hafnium with nickel and titanium. Shape-memory transition temperatures can be tailored from ambient temperature to >1000 °C depending upon the ternary alloy selected and the amounts of platinum, palladium, or hafnium added to nickel-titanium. Furthermore, martensite and austenite transition temperatures and alloy microstructure can be targeted through precipitation hardening via thermal aging. The work Sandia is conducting currently involves evaluating high-temperature shape-memory alloys and the shape-memory effect in bending configurations. Few studies exist in the literature regarding bending performance of high-temperature shape-memory alloys. This is significant in that most of the S&T safety and security applications that we foresee for Sandia's National Security Mission will require the alloy to be engineered in a bent configuration (e.g., actuator arm, spring, shutter, etc.). During the course of our work and through our collaboration with NASA GRC, we became aware of an alloy that exhibits > 90% two-way shape memory effect. Although the two-way shape-memory effect is undesirable for a one-time safety device, this discovery immediately offers the opportunity to create thermomechanical actuator devices that are activated at high temperature or through resistive heating for actuator applications. These approaches and associated research project will be the subject of a follow-on LDRD.

The accomplishments from FY 2011, subsequent year work, and related publications will result in a design guide for the S&T community to target alloy compositions and processing parameters for many other high temperature shape memory alloy applications.

It is our expectation and long-term goal that the results from FY 2011-2013 work will provide the foundation for a new growth opportunity, investment area, and expertise for Sandia, the nuclear weapons complex, and the DOE. The advantages and opportunities to create devices and components that enhance nuclear safety, security, and performance margins over existing approaches are abundant. Our partnerships with NASA's GRC, Los Alamos National Laboratory, and Texas A&M University allows Sandia to highlight our work to other government and academic institutions, to a broader scientific community, and to high visibility forums. This mission-relevant science program and its success will yield enduring collaborations and programs for the Laboratories.

New Composite Separator Pellet to Increase Power Density and Reduce Size of Thermal Batteries
151359

Year 1 of 3
Principal Investigator: L. A. Mondy

Project Purpose:
The separators in molten salt (thermal) batteries are produced by the slow, labor-intensive pressing of powder blends into pellets. There is a need to provide more functionality in a limited amount of space, leading to requirements for smaller and lighter batteries. Unfortunately, pressed separator pellets are too brittle if made thin, so battery stack heights are difficult to reduce while maintaining power output. We propose a novel manufacturing process for separators that will lead to significantly smaller battery stacks, improved performance, and decreased production costs.

We will develop novel thermal battery separators using self-assembling ceramic nanoparticles to form an internal microstructure with very high porosity and mechanical strength. The ceramic starts as an emulsion, where surface modified nanoparticles migrate to droplet interfaces forming flawlessly packed, interconnected struts that remain when the emulsion is dried and sintered. The new emulsion-based process must be engineered to meet the complex materials and compatibility requirements of the battery system including wetting properties, high dimensional stability, pore size and connectivity, and electrical impedance. Although similar processes have been shown to form exceptionally strong ceramics, no one has attempted to produce thin sheets needed for thermal battery separators. Pellets will be punched or cut from the sheets on demand, eliminating the slow pellet-pressing step. Despite the challenges, if successful, this process will provide a revolutionary means to increase the power density, improve manufacturability, and reduce the overall size and weight of molten salt batteries.

Summary of Accomplishments:
We have created proof-of-principle magnesium oxide (MgO) ceramics with very low densities and high porosity through three techniques. We were the first to create MgO ceramics using an emulsion templating technique pioneered for other metal oxides by Arkatuna et al., 2008. Extreme stabilization of oil-water emulsions was obtained with MgO particles that were surface-modified with short amphiphilic molecules, yielding emulsions that could be dried and sintered into strong ceramics. We have examined processing parameters and materials to determine the sensitivity to these parameters of the final pore size and strength. For example, various amphiphilic materials at various levels of pH were tested to determine the appropriate surface modification of the particles to allow creation of stable emulsions. Various amounts of oil, water, particles, and amphiphiles were tested, as well as the mixing method and energy. Sintering time and temperature were varied. Other advanced processes were also examined, including using pore formers and reticulated foam templates with ceramic slips made from MgO powders. Addition of polymers to enhance processability is examined in all processes. Scanning electron microscopy, mercury porosimetry, and hardness testing were also performed to compare ceramics made with the three techniques. Results show that the more standard ceramic techniques (using pore formers and foams) yield lower porosity materials than the emulsion techniques but that these materials may still be appropriate for thermal battery separators. Equipment to test the ionic conductivity of our prototype ceramics backfilled with electrolyte has been built, and testing has been initiated. The ionic conductivity is a key quality required for successful use of these new ceramic materials as thermal battery separators.

Significance:
This project provides a means for increasing the power density and for reducing the overall size of molten salt batteries. This project additionally builds a new base of scientific expertise and technical

capabilities relevant to the breadth of Sandia's mission areas, including expertise in advanced materials, diagnostics, and modeling. New fabrication methods for highly porous, mechanically robust ceramic foams will be useful for a wide variety of applications ranging from catalyst supports, filters for liquid metals, tissue engineering, high temperature thermal insulation, and lightweight structural supports.

Liquid Metal Environment Sensing Devices (ESDs)
151361

Year 1 of 3
Principal Investigator: P. C. Galambos

Project Purpose:
The purpose of this project is to create a novel microsystem and technology for environmental sensing (shock, acceleration, integrated acceleration) based on motion of a liquid metal (LM) drop (e.g., mercury or mercury/thallium eutectic for low temperature applications down to ï 61 ˚C) undergoing acceleration. The drop moves along channels under an applied g-load, and if the g vs. time profile matches the design profile, it will end up at a location bridging otherwise isolated contacts to switch on a circuit. This system has application to secure electrical switching for severe nuclear weapons (NW) environmental security device (ESD's) (launch accelerometers) and can be adapted for man-safety applications and non-integrating accelerometers (alternate Rolomite).

The novel microsystem being created is envisioned as a small electronic component. Drop size must be small to meet the microsystem requirement. This component development is challenging because surface forces dominate at this scale and we are relying on inertia forces to move the drop. In addition, there are significant materials compatibility and packaging challenges. For instance, mercury vapor amalgamates with gold and will rapidly consume a gold trace, rendering it nonconductive. Also for a predictable drop response to g-loads, the size of the droplet proof-mass must be tightly controlled, which is difficult at these scales. The droplet must be inserted into the channel in an oxygen-free environment to prevent electrode and drop oxidation.

These challenges require cutting-edge solutions. The challenge of low inertia at the microscale was addressed numerically (a commercial code, Flow3d, was modified to model this problem) and experimentally (centrifuge testing) using a unique microfabricated prototype channel design and assembly with Hg-compatible materials. This solution showed more-than-adequate g-sensitivity in the parametric design space modeled and first prototypes tested. A unique liquid metal (LM) channel filling system and procedure was developed for oxygen-free insertion of tightly controlled small-volume drops.

Summary of Accomplishments:
The accomplishments for the first year are as follows:

1. Prototype. First prototype ESD channels designed and fabricated in silicon on insulator (SOI) wafers. Channels were etched 125 microns deep in the SOI device side, and width varied from 450 to 125 microns. A unique Bosch etch technique was used to create fill holes in the SOI handle wafer and eliminate saw debris. The second-generation prototype has been designed and will be used to investigate the effect of controlled surface roughness and of posts and ridges of different sizes and spacing on drop motion.
2. Assembly. SOI channels were sealed with an epoxied glass cover containing electrodes. We also achieved effective glass attachment using an anodic bond, eliminating possible epoxy contamination. Various buried trace, wafer bonding, or glass frit methods can be used to establish a hermetically sealed cavity containing electrodes.
3. Channel Hg filling. A unique mercury fill system was developed using a syringe pump, a nanoliter 3-way valve, adhesive free nanoliter fittings, and pressurized nitrogen gas to insert microliter drops in channels.
4. Centrifuge testing. A microscope and video system were installed with the ESD on a centrifuge to provide continuous monitoring of the Hg drop motion as g-levels were increased. Drop motion occurred between 10 and 20 g's, in agreement with modeling.

5. Materials compatibility. Gold trace destruction and platinum trace survival upon mercury exposure were observed. Therefore, we will use platinum traces in future. Residue that was observed in channels was probably either epoxy or Au/Hg amalgam. Next ESD's should have no epoxy or gold.
6. Modeling. Modeling of channel geometry (2D and 3D) with drops exposed to a range of g-levels was conducted using Flow3d (commercial software) adapted for this surface tension dominated problem. Drop motion occurred from 3 to 30 g's depending on design details.

Significance:
This project ties to the DOE's nuclear weapons (NW) national security mission by developing novel ESD technologies with enhanced surety, reduced size, cost, and complexity, and by furthering the science and engineering foundation for nuclear weapons. This technology also has man-safety applications; as well as potential arming, fuzing, safety, and firing applications. This project ties to stockpile stewardship program (SSP) of the NNSA by potentially enhancing the security, reliability, and scientific understanding of a key NW component. The first NW insertion opportunity for a device based on this project might be a launch accelerometer for development flight tests or a shutoff switch for man-safety applications.

Other Sandia business areas that may benefit from this work include penetrator testing, acceleration, shock, vibration and load sensing, and conventional weapons ESDs. Applications in cyber security that might utilize a reconfigurable circuit architecture could be based on a liquid metal component. Radio frequency (RF) communications might also benefit from circuit designs that include a liquid metal circuit element.

Novel Failure Analysis Technique for Defect or Precursor Detection
152502

Year 1 of 2
Principal Investigator: J. Beutler

Project Purpose:
The ability to successfully detect and localize defects responsible for failure modes in integrated circuits (ICs) is critical in high-quality, high-reliability production. The novel failure analysis technique (NFAT) has the potential to extend these defect localization and screening techniques to advanced technology nodes. Sandia has been a world leader in developing many advanced failure analysis (FA) techniques to detect defects in ICs. However, the effectiveness of present FA techniques is declining as IC complexity increases. Often, electrical signals, such as excess leakage current and device functionality help identify a failing device. However, in state-of-the-art ICs, these failure modes can be masked by modes of normal operation by other transistors (100s of millions in advanced technology) on the chip. These normal modes of operation often overwhelm any defect mode. This limits the capability of existing FA techniques.

A crucial FA technology is energetic beam stimuli since it allows for localization of defects within an IC. Energetic sources such as laser beams are known to selectively enhance "failed" electrical signals of a defect and are the basis of many FA techniques. Coupling NFAT with energetic beam stimuli has tremendous potential. Conventional FA tools will provide a baseline to discover the effectiveness of NFAT as a standalone tool or integrated technology.

Summary of Accomplishments:
Simple ICs were evaluated using novel NFAT, damaged to varying degrees via accelerated testing, and reevaluated with NFAT to see changes in results. Before- and after-stress data were also taken with conventional FA tools and techniques such as parametric testing, light emission microscopy (LEM), light-induced voltage alteration (LIVA), and thermally induced voltage alteration (TIVA). In many cases, only a subset of conventional FA techniques revealed an induced change in the IC due to accelerated testing. In each of those cases, NFAT also detected that change. Typically, accelerated damage to an IC was only detectible by testing the IC beyond the devices' manufacturers' recommended maximum specifications (something that would not be done in prescreening); however, NFAT was able to successfully detect these anomalies without exceeding these specifications.

Preliminary work that couples NFAT with beam-based localization techniques shows that NFAT localizes defects, which conventional techniques do not. Whether this indicates a genuine defect region is yet to be determined and is a focus thrust for the second year's work.

Significance:
Many systems require complex, highly reliable microsystems to ensure success. Successful implementation of NFAT will give these programs a powerful and inexpensive tool to perform quick, cost-effective FA that may not be possible or is more difficult to implement presently.

Imaging and Quantification of Hydrogen Isotope Trapping in Stainless Steels
152506

Year 1 of 2
Principal Investigator: R. A. Karnesky

Project Purpose:
Hydrogen isotope transport through and embrittlement of pressure vessels ultimately limit component lifetime. Understanding hydrogen interactions with structural materials requires knowing not only equilibrium properties (temperature-dependent lattice solubility, diffusivity, and permeability of hydrogen), but also transient properties. Because it enhances local hydrogen concentration, defect trapping greatly reduces fracture toughness and changes deformation properties. It also makes the apparent diffusivity of hydrogen many orders of magnitude different from the equilibrium lattice diffusivity. However, trapping is typically a weak point in current simulations. Usually, only a single trapping mechanism is assumed, while multiple trapping mechanisms operate in real microstructures at temperatures of interest. The experimental characterization of trapping has been limited and has focused on high-strength ferritic steels. Austenitic alloys that are candidate materials and have lower equilibrium permeability values for hydrogen have not been analyzed as deeply. While the trapping at large features, including grain boundaries and incoherent particles, has been imaged indirectly, smaller features (e.g., precipitates and solute atoms) have not been studied in detail due to fundamental resolution limitations of most analysis techniques.

The location of hydrogen isotopes will be imaged in austenitic stainless steel using local-electrode atom-probe (LEAP) tomography, and trapping energies will be measured by thermal desorption spectroscopy. LEAP tomography has sub-nanometer resolution and excellent compositional sensitivity due to pulse-counting techniques. Site-specific sample preparation is possible using a focused ion beam, and model materials can be used to characterize trapping at low-number-density features. These unique capabilities of LEAP tomography make it promising for the study of hydrogen isotopes, but it has not yet been used to image trapping in austenitic stainless steels. The experimental work will be compared with first-principles calculations of the binding energy of hydrogen isotopes to solid solution elements in stainless steels and to coherent precipitate/matrix interfaces.

Summary of Accomplishments:
We have observed deuterium, for the first time, using local-electrode atom-probe tomography in stainless steel and model ultra-fine-grained aluminum specimens. Protium replaced deuterium during electropolishing in large ratios, so we have polished tips of 21-6-9 stainless steel with varying nitrogen content and have charged them with high-pressure deuterium gas. We will also attempt electropolishing with deuterated acids.

We have measured deuterium-trapping energies in 21-6-9 stainless steel and 304 stainless steel using thermal desorption spectroscopy.

Model samples of grain-boundary-engineered nickel have been prepared by deuterium charging, characterizing grain boundaries, and focused-ion-beam milling from these boundaries. Atom-probe tomography will reveal why the fracture properties of these engineered alloys differ substantially from as-received nickel.

Significance:
A detailed understanding of hydrogen-isotope transport in structural materials will help in the design and service of gas-transfer-system (GTS) reservoirs and materials for energy generation, storage, and

transport, including fusion and other renewable energy and energy security programs. Future opportunities for continuing this work through NNSA, DOE Energy Efficiency and Reusable Energy, or industrial partnerships are anticipated.

Developing a Multiscale Test Approach for Characterizing NW Polymer Composites
154058

Year 1 of 2
Principal Investigator: T. Briggs

Project Purpose:
The purpose of the project is to generate a significant increase in the knowledge base of nanoparticle interaction and energy-absorbing deformation and fracture processes as a result of the presence of nano-reinforcement. The effects of doping a traditional fiber-reinforced composite material system with nano-reinforcement on deformation and failure will be understood from particle-matrix adhesion up to macroscopic fracture. In addition, the depositional process for dispersing nanoparticles onto a secondary substrate will be studied and understood.

Advanced fiber-reinforced nanocomposites (FRN's) are being seriously considered for Sandia applications due to their potential to enhance mechanical performance and reliability. However, as a result of the multiple constituents comprising FRN's, load distribution, deformation, and subsequent failure mechanisms are unknown. The alignment, adhesion, functionalization, spatial distribution, and aspect ratio of the nano-reinforcement fibers are all coupled in an unknown, multifaceted manner, yet they are vital for structural composite applications. These material aspects all affect the material's ability to carry external loads and to dissipate energy through fracture processes and introduce a new set of scientific challenges in understanding FRN behavior. In order to confidently employ FRN's, the strong dependency of material behavior on the complex collection of material parameters needs to be rigorously studied. To address these issues, we propose an experimental program to obtain a fundamental understanding of advanced FRN's, which are expected to demonstrate new response behavior for design.

Summary of Accomplishments:
First, we have established effective electrospinning process parameters through an iterative procedure in order to homogenously disperse the nano-enhancement onto the composite laminas. These parameters include the solution flow rate, electric potential between tool surface and needle, standoff distance, rastering velocity, and drum revolutions per minute (RPM).

Second, the baseline and nano-enhanced composite materials have been designed, laid-up and consolidated, ready for specimen cutting and fabrication, with mechanical testing to follow. In addition, the capabilities for cutting nanocomposite materials have now been developed with a new shop set-up consisting of a wet diamond blade saw and a high-efficiency particulate air (HEPA) vacuum system to remove airborne particles, as required by the ES&H on-site industrial hygienist. Currently, the ability to handle the waste generated from the cutting process is being defined with ES&H and the facility personnel are scheduled to install the required hardware for vacuum filter and blower assemblies to complete critical tasks for the next steps.

Third, the surface characteristics and topological implications to the electrospinning deposition process have been both qualitatively and quantitatively investigated. Through the use of optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), and profilometry, the extent, orientation, and homogeneity of the electrospun fibers, as well as the resulting surface roughness parameters, has been defined. Also, the effects of cutting the composite materials with the diamond saw blade have been investigated using optical surface profilometry with a key concern being the induced surface roughness, which introduces geometric discontinuities serving as stress concentrations during the mechanical performance evaluation to come.

Last, a paper entitled, “A Novel Method for Homogenous Dispersion of Multi-Walled Carbon Nano-Tubes onto Prepreg Composite Materials” is currently being written.

Significance:
Future and current Sandia systems of interest are constantly under scrutiny to be improved and made more efficient for long-term mechanical reliability. This proposal targets innovation for Sandia core mission needs through more reliable, fracture-resistant nanocomposites engineered to meet performance requirements. The DOE has numerous applications that would benefit from this enhanced understanding of nano-reinforcement, such as the protection of critical electronics within packaging subject to high shock, vibration, and transverse impact. The fundamental science developed to design more failure-resistant and reliable nanocomposite materials will benefit a variety of core product lines, in addition to countless other national security applications.

Exploring Formal Verification Methodology for FPGA-Based Digital Systems
154691

Year 1 of 2
Principal Investigator: Y. Hu

Project Purpose:
With the Life Extension Programs (LEPs), many nuclear weapon (NW) electronic components are being replaced by modern digital devices, increasing system complexities dramatically. The capability of ensuring the reliability, security, and robustness of these upgraded systems is of great interest. Custom hardware systems are designed and utilized throughout the NW operations space, from controller devices on the weapons to telemetry systems on Joint Test Assemblies (JTAs). These designs commonly rely on the use of Field-Programmable Gate Arrays (FPGAs) to implement sophisticated logic. Effective verification, while increasing confidence, can reduce the overall effort in system debugging and testing.

The purpose of the project is to discover a novel way to apply formal verification (FV) to digital designs in NW applications. This is because random simulation cannot be guaranteed to cover the entire event space of a design, and formally verifying designs to meet NW quality standards remains an engineering challenge.

FV emerged as an alternative approach to traditional random simulation and directed testing techniques for ensuring correctness of hardware designs. While FV has been successful in many applications, such as aircraft navigation systems, cryptography, and medical devices, there has been little work at Sandia in this field for NW-related hardware systems. This project will initiate the leveraging of FV for high-consequence systems in NW space.

We are developing of trusted FPGA-based hardware designs through the use of novel FV algorithms. Once implemented, the algorithms will perform domain-specific verification at different phases of FPGA design (synthesis, place and route, programming netlist generation) for high-assurance applications, such as surety and telemetry. The verification algorithms developed will support the analysis of critical digital components, such as memory and transceiver blocks, with mathematical reasoning from automated theorem proving and model checking. Such verification will detect race conditions and corner cases at an early stage, eliminating system failure and instability during operation.

Summary of Accomplishments:
We have done extensive research of FV in mission-critical, high-consequence applications which will lead to a publication. We have analyzed several case studies (e.g., National Aeronautics and Space Administration [NASA's] aircraft controller) that demonstrate the effectiveness of FV.

To build up the expertise in this field, we have attended several conferences to learn more about the most up-to-date S&T in the field. Several industrial leaders in FV such as Mentor Graphics were invited to give on-site presentations. We have also established external interactions with the Formal Methods Group in NASA, NEC Laboratories America, and Princeton University.

Within Sandia, we have brought this S&T to the attention of several organizations that focus on digital system designs with FPGAs or application-specific integrated circuits (ASICs). Through the effort of a NW Cyber SecurityWorkshop, we demonstrated what FV can achieve with prototypical examples.

We have investigated popular tools (open source and commercial) for formally verifying FPGA-based designs. Each of them has advantages and disadvantages, with none that is tailored for NW specific requirements. We have created a novel decomposition approach for random access memory (RAM) to solve the state explosion problem imposed by model checking. By combing automated theorem proving and model checking, we demonstrated that a RAM of any size can be formally verified.

We have elaborated several proposals for integrating an existing event-driven simulator (Orchestra) with an advanced symbolic model checker (NuSMV) to meet this vision of Sandia's future digital design methodology. The candidates include: 1) implementing basic model checking technique into Orchestra and 2) generating Orchestra models for various logic blocks and providing an API to NuSMV's model checker.

Significance:
Digital systems used in DOE's mission areas have extremely high requirements for reliability and security. Being able to formally verify these systems before actual operation will be critical. Formal verification techniques, if applied successfully, can detect design flaws at a very early stage. Recognizing the extreme levels of reliability and security needed in the NW space, we propose to leverage this science and technology to deliver verified FPGA-based hardware designs for systems in DOE's mission areas. The formal verification techniques developed will increase the confidence level for high-assurance and high-consequence systems that are used in DOE's mission applications.

We are developing an integrated approach to testing, assessing the limitations of simulation while also introducing methodologies for formal verification, that is, the static analysis of all possible system states. With an open-source symbolic model checker known as NuSMV, we demonstrated the limitations of formal verification for FPGA designs involving memory. Such designs experience the state explosion problem, which renders extremely long run times or in some cases, makes components completely impossible to model efficiently. Although formal verification methods can reveal potential faults that simulation might miss, there are also issues with formal verification, in that such system complexity (with a very large number of states) is also an issue. Hence, we are now pursuing a design decomposition approach, seeking a methodology to decompose the system into a number of smaller pieces, such that these more manageable chunks can be more readily formally verified. This, of course, makes it necessary to demonstrate that all formal verifications of the decomposed system are still valid when the pieces are re-integrated into the entire system. A first case study of this type has been successful.

This research could enable a new approach to designing digital NW components where formal verification is built into the design process. This would make surety a guarantee along with the functionality of the design. If this project is successful, it will establish a foundation in the NW space for formal verification methods, especially for high-assurance applications, such as surety and telemetry systems. Given the cost and level of effort that goes into traditional analog systems, formal verification of digital systems will be attractive and beneficial. When digital systems are delivered, a high level of confidence can be expected if they are verified formally rather than through simulation based on random test vectors. This work will also enable Sandia to leverage an increasingly important science and technology into its NW mission.

Formal verification can also be integrated into the design and test flow of various LEPs. Such verification will help to detect hardware run-time race conditions and corner cases at an early stage, eliminating FPGA system failure and instability during operation. It will be beneficial to the NW space if harmful errors can be eliminated through formal verification without compromising design goals.

A Novel Bi-Functional Conducting Polymer Sensor Material
154762

Year 1 of 2
Principal Investigator: M. Kane

Project Purpose:
The purpose of this program is to design, optimize, and build a prototype of a conducting polymer sensor that is able to detect locally applied heat and locally applied chemicals. Conducting polymers such as a polyaniline (PANi) and polypyrrole (Ppy) are known to be sensitive to both heat and chemicals by differing mechanisms. Applied heat will change the rate at which charge transfer will occur (and density of charge carriers) and applied chemicals will swell the polymer, thus changing the charge transfer structure and homogeneity of the system. Both of these mechanisms lead to large changes in conductivity or surface resistivity. This behavior can be easily measured by the input of a small current or voltage and measuring the output voltage or current. Small, embedded electrodes that can be built into the sensor will be used for this purpose.

Most literature data contains only empirical results for conducting polymers at the temperatures of interest or modeling data at very low temperatures, which are not relevant to this work. This program seeks to understand the mechanisms of charge transfer at elevated local temperatures and exposure to chemicals that have not yet been explored by others. These findings will aid in the development of a sensor that has many applications within the DOE.

Summary of Accomplishments:
- Density Functional Theory (DFT) modeling was used to model the band gap and electron density within the conduction band of several polymer-dopant combinations. Polyaniline was chosen as the target polymer due to a very small band gap. Dodecylbenzenesulfonic acid (DBSA) was chosen as the dopant due to the potential for high conductivity.
- A process was optimized for the synthesis of PANi-DBSA that is soluble in common organics, such as toluene and xylene. This is very important as it allows processing of the polymer into a castable film. Standard synthesis procedures yield a practically insoluble powder, but higher conductivity. In this case, some level of conductivity was sacrificed for ease of processing.
- It was determined that the final synthesis product must go through some post-synthesis washing to remove excess reactants and water. Ethylene glycol was chosen as the wash solution and was shown to improve conductivity of the PANi-DBSA solution by over two orders of magnitude from the unwashed product.
- The PANi-DBSA films were characterized by atomic force microscopy (AFM), UV-Vis spectroscopy and scanning electron microscopy (SEM). The optical properties reflect those known for doped polyaniline.
- A custom microfluidics flow cell with patterned micro heaters and thermometers has been designed and fabricated. The exposure cell allows for in-situ measurement of conductivity and optical properties while heat and chemicals are locally applied to the sensor surface.
- Kelvin-probe measurements taken of the conductivity of the synthesized PANi-DBSA films revealed an interesting hysteresis when cycled between room temperature and elevated temperatures (400 K). This phenomenon has not yet been reported in the literature.

Significance:
The results of this project will greatly benefit the mission goals set by DOE's Strategic Plan. This study is also of academic importance since the mechanisms for changes in charge carriers within the conducting polymer due to locally applied heat and chemical exposure as compared to long range (bulk)

exposure are investigated through modeling and experiment, which has not been previously reported in the literature. Additionally, new processing methods for soluble conducting polymers have been developed that can benefit many alternative energy industries that use this type of material (e.g., photovoltaics, organic light-emitting diode (OLEDS), supercapacitors, etc.).

Ultrafast Laser Diagnostics to Investigate Initiation Fundamentals in Energetic Materials
154813

Year 1 of 3
Principal Investigator: D. Farrow

Project Purpose:
Currently, the chemistry of shock ignition in energetic materials is poorly understood. Models are purely empirical, and no direct measurement approach for probing the thermochemical environment within a shocked material currently exists. The shock initiation of energetic materials progresses on picosecond time scales behind the shock wave, and there exists a complex feedback between chemical and mechanical processes (changes in temperature, pressure and particle velocity) that determine the dominant pathways of ignition chemistry. Sandia currently possesses tools for measuring some mechanical properties during this process but does not have a diagnostic to follow thermochemical evolution during ignition. The extreme temporal and spatial resolution required to monitor the ignition process makes development of appropriate experimental tools a significant technical challenge. In this research, we propose to exploit recent developments in femtosecond laser spectroscopy to probe the evolution of temperature and critical chemical species on picosecond timescales in both the gas and solid phase of shock-initiated energetic materials. Using time-resolved Coherent Anti-Stokes Raman Spectroscopy (CARS) and other Raman-based techniques, we propose to directly measure the material temperature and chemical-reaction dynamics behind the shock wave. Capturing the relevant physical processes will require us to deliver measurements with both extreme temporal and spatial resolution (picosecond and micron scales) in a hostile environment where response to the ultrafast Raman probe is rapidly evolving during the measurement. Time-resolved temperature measurements have never been accomplished in a reacting or inert solid material under shock loading at temperatures and pressures typical of initiation. Time-resolved measurement of chemical composition during initiation of energetic materials would provide information about the performance of energetic materials used in the nuclear weapon (NW) stockpile and enable a transition from empirically based models to physics-based predictive simulation. This project will provide Sandia with an experimental capability that is at the forefront of the science of energetic materials, while directly addressing programmatic needs in support of NW.

Summary of Accomplishments:
We have set up and demonstrated two different single-shot techniques for measuring nitrogen gas temperature in flames. We have taken spectra of air and nitrogen gas at room temperature and have taken preliminary spectra of nitrogen in a heated gas jet using the first technique and single-shot room temperature data using the second. The latter method shows phenomenal signal to noise and shot to shot reproducibility. Early experiments and modeling using the first method suggest that sensitivity to phase fluctuation in the wings of the probe field will make implementation of this method in thin films very difficult, so we will proceed with the first method in flames. We have also finalized the design of a pulse shaper to stretch femtosecond pulses to use in shock formation and single shot dynamic ellipsometry probes of particle velocity, and we have begun set up of the ultrafast dynamic ellsipsometry experiment. We are also setting up CARS in single crystal semiconductors (GaN) to determine which methods work best for measuring temperature and chemical species in thin film explosives under shock.

Significance:
The experimental tools and methods are aimed at providing the first-ever direct measurements of chemical kinetics and temperature evolution during initiation of energetic materials critical to the stockpile. This new capability will provide Sandia with the ability to test new materials under a range of

shock conditions and to characterize the performance of aged materials. It will allow future development of predictive shock models that explicitly address ignition chemistry and spatial/temporal variations in ignition processes in a rigorous manner, thereby improving upon current empirical approaches.

Ion-Induced Secondary Electron Emission and Surface Flashover Breakdown for High Gradient Ion Beam Accelerators
155409

Year 1 of 3
Principal Investigator: J. S. Howard

Project Purpose:
The purpose of this project is to develop a set of data for ion-induced secondary-electron emission (SEE) and vacuum flashover that correlate directly to the materials and beam characteristics present in compact, portable, high-gradient particle accelerators. Such accelerators are important to nuclear weapon and other homeland security applications for the purposes of neutron and x-ray production. SEE, initiated by both electrons and ions, is an underlying mechanism for several failure modes observed with particle accelerators. Ion-induced SEE is relatively complex, and no data exist for ion-induced SEE and vacuum flashover that directly correlate to the materials and beam chemistries used in practical accelerators. The development of such data should lead to design improvements, allowing such accelerators to operate more reliably, efficiently, and productively.

The primary challenge to collecting these data is that the necessary experiments require an accelerator design that utilizes modern, compact ion sources and operates with variable perveance while maintaining consistent beam chemistry. The end goal for this project is the development of the ion-induced SEE data set, but the exercise of producing a variable-perveance accelerator is a significant challenge that is an important result in itself.

Summary of Accomplishments:
The significant accomplishments made to date have involved the following two areas: 1) developing the high-voltage pulse power system required for the experiments, and 2) learning particle-trajectory software to model and design the variable-perveance ion-beam accelerator. It was initially anticipated that the pulse-power requirements could be met by restoring a high-voltage system that was currently available but non-operational. Unfortunately, that task was too imposing without appropriate, dedicated technical support. Therefore, two smaller alternative pulse-power systems were designed, modeled, and built. A high-voltage chamber, capable of utilizing either setup, has been constructed and subsequently approved by ES&H. Preliminary tests have been done to verify the output waveforms; testing on actual samples is anticipated to start soon.

Becoming proficient with the particle-trajectory software has involved a significant learning curve. There are four primary aspects of using this software, each requiring significant effort to master: 1) creating model geometry, 2) assigning materials and boundary conditions, 3) solving for electromagnetic fields, and 4) solving for particle trajectories. A 2D software version was used initially to acquire general proficiency with the Computer-Aided Engineering (CAE) environment. By using simple 2D geometries with rotational symmetry, we demonstrated the general principal of operating an accelerator with variable perveance (constant current over a range of accelerating voltages). However, some physical constraints of the experimental setup will likely require asymmetrical accelerator geometry. Hence, we require a more sophisticated 3D model. Ironically, the lack of appropriate ion-induced SEE data, which is the focus of this project, is a significant impediment to providing an accurate model. Several 3D models are currently being analyzed to determine a final accelerator design.

Significance:

This project will impact research for portable, compact, high-gradient ion accelerators. SEE is a general consequence of impacting material surfaces with high-energy particles; unfortunately, this mechanism can produce unwanted effects that may cause failure of high-gradient accelerators. In some ion accelerators, it is generally necessary to devote some fraction of the accelerator volume to suppression of ion-induced secondary electrons. It is likely that the traditional implementation of this design requirement has involved excessive precautions. Most existing data on ion-induced SEE involve monatomic, single-charge species ion beams impacting very common materials (Ag, Al, Cu, etc.). Since SEE data do not generally exist for impure ion beams with multiple charge species impacting unique materials, it is customary to find an approximate beam-material interaction and extrapolate the worst-case SEE, generally by an order of magnitude or more. The volume and bias required for secondary electron suppression ultimately cuts into the volume and voltage available for ion acceleration; hence, being overly cautious on suppression reduces the efficiency and output the accelerator can achieve. Of course, we will also be searching for any beam-material interactions that produce unusually high levels of ion-induced SEE, as SEE tends to reduce reliability and efficiency of high-gradient accelerators. In short, we hope to advance the design of portable, compact, high-gradient accelerators by enabling them to run more reliably, efficiently, and productively.

Determination of Reaction Zone Length in Vapor-Deposited Explosive Films
156704

Year 1 of 3
Principal Investigator: R. Knepper

Project Purpose:
The purpose of this project is to determine reaction zone lengths in explosive materials by precise manipulation of the confinement conditions. Reaction zone length is a key parameter in modeling explosive behavior. However, many important explosive materials have very small reaction zones that are extremely difficult to measure using standard techniques. In this project, we propose a new method for determining reaction zone length at micron to sub-mm scales by varying the confinement conditions.

While effectively infinite confinement is known to cause a decrease in the critical thickness and an increase in detonation velocity with increased shock impedance, the thickness of confinement needed to become "infinite" and the magnitude of the effect on detonation velocity and critical thickness are largely unknown. An empirical model will be developed during this research that will not only elucidate this relationship, but also provide insight into the structure of the detonation reaction zone by using confinement conditions (thickness, shock impedance) to give an indirect measure of the reaction zone length.

This work is novel, as there has not previously been a reliable method for measuring reaction zone lengths at sub-mm scales. Research will focus on explosive materials that have a critical thickness for detonation less than ~ 200 microns, which are likely to have very short reaction zones. Both explosive and confinement layers will be vapor-deposited to provide precise control over layer thicknesses and microstructure. Vapor deposition also promotes intimate contact between the explosive and confinement layers, creating a well-defined model system that can be easily incorporated into mesoscale computer simulations. Vapor deposition readily accommodates various film geometries by using shadow masks during deposition, allowing geometrical effects to be studied as well.

Summary of Accomplishments:
Over the five months this project has been active, we have begun to investigate various methods of depositing metal layers onto explosive films. We have determined that electron beam evaporation is the best method currently available, as it generates less heat than thermal evaporation (which can lead to degradation of the explosive) and emits atoms with less kinetic energy than sputtering (which can cause metal atoms to embed themselves beneath the explosive surface) while maintaining a high deposition rate. At this time, we have successfully deposited aluminum layers onto pentaerythritol (PETN) and hexanitroazobenzene (HNAB) films, and early experiments suggest that we will be able to deposit copper layers onto HNAB as well.

Preliminary microstructure and thermodynamic analysis of candidate explosive materials (including PETN, dinitrofurazanfuroxan (DNTF), hexanitrostilbene (HNS), and HNAB) has led us to concentrate our first set of experiments on HNAB due to the extremely low surface roughness inherent to vapor-deposited films of this material and its fairly high melting point, both of which will facilitate an abrupt interface between the explosive and confinement layers. Baseline experiments (confined only by materials with a shock impedance lower than that of the explosive) to determine critical thickness for detonation and detonation velocity have been performed for HNAB films, indicating a nominal detonation velocity of ~ 7.38 mm/us and a critical thickness for detonation of ~ 117 microns.

Significance:
Knowledge of reaction zone lengths for various explosives under different confinement conditions will greatly enhance the predictive capabilities of next-generation computer simulations. The empirical model developed will allow one to engineer confinement conditions to produce desired detonation velocities and reduce the amount of explosive needed, providing enhanced reliability, reduced cost, and limiting collateral damage in devices. Capping explosives with vapor-deposited metal layers may also enhance stability by inhibiting surface diffusion that could otherwise lead to coarsening of the grain structure during aging. In addition, the incorporation of metal layers could promote new initiation techniques, such as direct optical initiation.

This work benefits Sandia's Nuclear Weapons mission. Utilization of microenergetic components, fabricated by modern microelectronic methods, has the potential to increase the precision, reliability, surety, and safety of current and future weapon systems. This work addresses key deficiencies in our understanding of energetic material behavior at the mesoscale, and these experiments should benefit ongoing predictive modeling efforts. It will create the foundations to define a path for integration of microenergetics in weapons systems.

Gas Permeation Properties of Graphene Membranes
158183

Year 1 of 3
Principal Investigator: L. Biedermann

Project Purpose:
Separation of hydrogen isotopes from helium is of interest to Sandia and other DOE labs. One established method to achieve high-purity hydrogen filtration uses palladium-silver membranes, which are expensive and sensitive to surface contamination, resulting in degraded performance. Graphene membranes offer a promising alternative to current membrane technologies since a single monolayer of exfoliated graphene is impermeable to helium at room temperature, yet hydrogen intercalates epitaxial graphene to bind to SiC at elevated temperatures [Bunch 2008, Riedl 2010]. Furthermore, graphene can be fabricated on a commercial scale and transferred to a variety of substrates.

This project will investigate how gas permeation through graphene may be optimized by careful design and assembly of graphene membranes. Exfoliated graphene, which is the highest quality form of graphene, is impermeable to helium and larger gases at room temperature and can withstand pressure differences up to 600 kPa (Bunch, 2008). Density functional theory (DFT) simulations (Jiang, 2009, Blankenberg, 2010) confirm that gasses cannot permeate through graphene's benzene rings. However, hydrogen can intercalate epitaxial graphene at 600-1000 ˚C; grain boundaries and Stone-Wales defects are likely permeation pathways (Riedl, 2010).

Investigation of permeation through chemical vapor deposition (CVD)-grown graphene and reduced graphene oxide (RGO) will allow us to determine how intrinsic properties of these graphene sources, such as grain sizes and the presence of defects and grain boundaries, affect the permeability. CVD-graphene and RGO were selected since they are commercially scalable, easily transferrable forms of graphene, unlike exfoliated or epitaxial graphene. To evaluate the utility of graphene as a selective membrane, permeation of various gases and gas mixtures will be measured.

We will develop methods to fabricate high-quality graphene membranes on porous substrates and will determine under what temperature and pressure conditions graphene is a permeable membrane. Development of an alternative mechanically robust permselective membrane will directly benefit the Nuclear Weapons area.

Summary of Accomplishments:
Since the project start in late June 2011, work has focused on developing a reliable method to transfer graphene and assembling a vacuum system to measure the permeability of the transferred graphene films. We have transferred ~30 samples of chemical vapor deposition (CVD)-grown graphene from the Cu foil on which it was grown to target SiO_2/Si and SiN/Si substrates. To accomplish this, we protect the graphene with a spun-on polymer (PMMA) handle, dissolve the underlying Cu foil in an aqueous etchant, adhere the PMMA/graphene stack on the target substrate via van der Waals forces, and remove the PMMA handle. Optical and atomic-force microscopy confirm that the graphene was transferred and highlight the importance of a robust, yet easily removable, polymer handle to protect the graphene film during transfer. Increased PMMA cure time (few days) minimized swelling and cracking of the PMMA during the etching process. Both ammonium persulfate and iron nitrate were used as etchants; agitation and higher concentrations of iron nitrate decreased the etch time, better preserving the PMMA/graphene film. We developed a technique to gradually drop the film onto the target substrate by slowly removing the surrounding water bath. Optimization of this technique allows us to transfer graphene films without

folding. The PMMA handle has been removed using organic solvents; experiments to remove the PMMA by baking in air are ongoing.

A custom vacuum system to measure the permeability of the graphene films is almost completed. This system consists of two chambers, one ultra-high vacuum and the other variable pressure, separated by a gate valve, on which graphene films will be mounted for permeation measurements. Two turbomolecular pumps backed by roughing pumps can independently pump the chambers. Ion and capacitive manometer gauges will monitor the pressure.

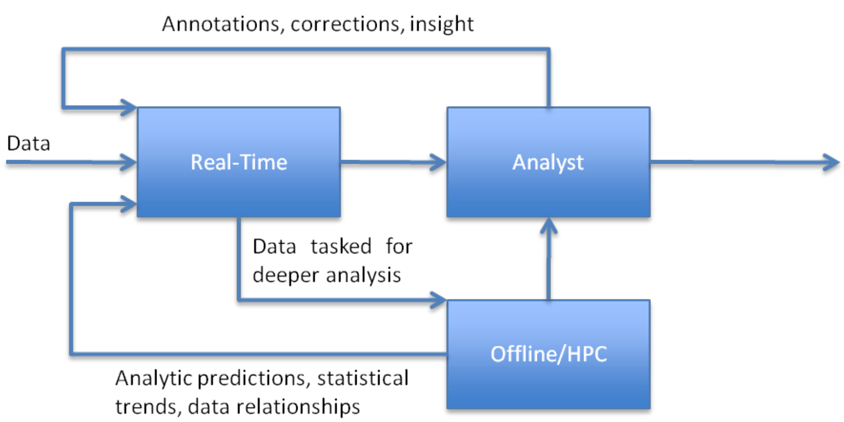
Significance:
Storage and transfer of hydrogen isotopes with minimum contaminating species are of great interest to Sandia. Membranes which filter hydrogen isotopes would also benefit tritium processing. Also, filtration of H_2 from CH_4 is of interest to the DOE Office of Fossil Energy, which is currently funding membrane research to further production of hydrogen from steam reforming for fuel cell applications.

CYBER SECURITY INVESTMENT AREA

This investment area funds projects designed to improve all aspects of secure computation, including desktop, network, and supercomputing aspects of Laboratories and DOE complex operations. This includes both hardware and software projects that hold potential for improving operational capabilities and those designed to detect and thwart malware intrusions into secure and critical cyber systems.

Hybrid Methods for Cyber Security Analysis
Project 154197

An increasingly sophisticated and ever-evolving set of cyber hackers and intruders poses a large threat to all secure cyber systems, including those of Sandia and other institutions in the DOE complex. This project is attempting to assist human analysts parse through the enormous streams of data that must be examined to detect malware intrusions by developing a real-time network capture and analysis software framework that is modularized and flexible to the extent that as new tools are developed, they can be "swapped" into the framework. Additionally, it places the human analyst in a position whereby s(he) can facilely analyze data in real time, online, and/or employ large-scale offline methods such as graph algorithms and text analysis, with the insights gained from those analyses fed back into the real-time analytical software to improve its detection capabilities in an ongoing fashion.



The combination of real-time, offline HPC, and human in the loop will be critical for responsive and agile network defense.

Cyber Security Investment Area

Hybrid Methods for Cyber Security Analysis
154197

Year 1 of 3
Principal Investigator: B. N. Wylie

Project Purpose:
The discovery of threats in computer networks is a critical task in cyber security. Because of the volume and complexity of the data, most deployed methods rely on signature detection and simple statistics and are guided more by time and hardware constraints than by the needs of the problem. This gives an adversary many degrees of freedom within which to hide.

We are conducting research that will broaden analysts' views and deepen their capabilities with respect to the always-on torrent of data. We will bridge real-time tools and compute-intensive HPC algorithms by allowing the "human in the loop" to transfer insight freely between on- and offline capabilities, thus continually refining their ability to automatically analyze incoming data. We will specifically address the problem of malicious email detection, with the goal of moving beyond simple signature detection to accurately identify mutations or variations of malicious email attacks.

The challenge of placing the analyst at the center of advanced capability consists in casting each algorithmic component as part of a coherent, accessible whole. Our work will fuse real-time techniques (rule-based intrusion detection and frequent item set analysis) with large-scale offline methods (graph algorithms, text analysis and statistical modeling). At a high level, this requires model and data fusion as we enlist diverse algorithms in support of cyber security. We find a corresponding engineering challenge as we federate diverse software into a coherent system. Our innovation lies in integrating these parts into a whole that can affect and be quickly affected by expert users and decision-makers.

Summary of Accomplishments:
The initial focus of this project has been to develop real-time detection of email messages with attachments containing malicious software or hyperlinks. A cross-laboratory team has been assembled for this project which is essential for Sandia to take a leadership role in the design and development of network defense capabilities against an increasingly sophisticated set of adversaries.

In our first year of work, a real-time network capture and analysis software framework has been developed and is now being evaluated. The framework currently consists of software modules for: 1) real-time email packet capture and sessionization, 2) header and content data modeling, 3) email clustering and classification, and 4) visual exploration of potential threats in email messages or groups of messages. A key milestone for the project was integrating the new analysis framework into Splunk® (a product of Splunk, Inc.), one of the key search and analysis tools currently being used by network administrators and cyber security analysts at Sandia.

Significance:
The project objectives — including quick detection and attribution of attacks, software development to ensure integrity of our cyber infrastructure, and threat analysis methods based on scalable informatics — are well aligned with Sandia's strategy.

The modular nature of this framework enables researchers and analysts to explore new approaches to detecting malicious network events by simply swapping in new technologies as they are developed. For example, packet capture currently is accomplished using either Lawrence Berkeley Laboratory's Bro software or a proprietary tool developed through a Sandia Work for Others project, and switching between the two methods does not impact analysis or data flow in other parts of the framework. Such extensibility is critical in developing effective solutions for the ever-evolving nature of network attacks.

With this new framework in place, advanced analytic methods can be deployed to analyst desktops and incorporated into their workflows seamlessly, paving the way for future collaboration between key federal organizations involved in cyber security.

Investigate the Effectiveness of Many-Core Network Processors for High Performance Cyber Protection Systems
154198

Year 1 of 2
Principal Investigator: U. Onunkwo

Project Purpose:
Network Intrusion Analysis Systems (IAS) and cyber protection devices, such as stateful firewalls, are not keeping up with the explosive growth in network bandwidth. Most of today's systems are barely able to keep pace with network traffic of one gb/s. Currently, enterprises are moving their networks to 10 gb/s bandwidths with near-future aspirations of 40 gb/s. These high-bandwidth networks require smarter and more efficient ways for enabling cyber protection to keep pace.

New algorithms for detecting anomalous behavior in streaming network traffic are being developed that significantly improve the probability of detecting nefarious behavior over the traditional techniques of detecting static signatures or patterns. However, these advanced behavioral analysis techniques require significantly more computational capabilities than static techniques. Moreover, many locations where IASs or firewalls are deployed have limited power, space and cooling resources. This makes the use of traditional large computing systems impractical for the front-end systems that process large network streams.

We must rethink firewall implementations, specifically stateful firewalls, on high-data-rate networks. This process should not only demonstrate high performance, but also be easily adaptable and rapidly reconfigurable to keep pace with the ever-evolving nature of cyber attacks. In this project, we are applying modern many-core processors to solve this problem. We will develop a 10gb/s stateful firewall on a Tilera 64-core system to investigate the effectiveness of stateful firewalls on these new processors. Using many-core systems for 10 gb/s may be too ambitious, but demonstrating effective solutions moves us towards a better cyber protection stance.

Summary of Accomplishments:

- We ported a stateful firewall code (iptables) to a Tilera many-core system, which involved building a Linux kernel module (netfilter) into the default TILEPro™ kernel and building user-space iptables code. This has also been demonstrated to be functional on a single core.
- We developed a ring-buffer-based packet distributor with fast packet hashing functions for both the Intel and TilePro systems. This guaranteed that session states were maintained correctly across firewall processing pipelines and is undergoing optimizations.
- We developed a number of "passive-wire" methods that make our firewall machines robust. These methods exchange packets between network interfaces on our firewall-hosting machine, where the interfaces are configured without Internet protocol (IP) addresses. This code serves two purposes: 1) secure communication by ensuring packet exchanges between zones (networks) always pass through our firewall, as well as 2) guaranteeing that the system running the firewall can only be accessed via console, thereby eliminating opportunities for it being hacked over the network. The code is passive because users between zones are ignorant of its existence while being protected by the stateful firewall.
- We created the user-space fast interprocess communication code for Tilera many-core processors. This code sends arbitrarily sized packets between firewall tasks without going out to shared memory, thereby reducing contention in nonuniform memory and providing higher performance via cache. This code has been ported to kernel-space, but is still undergoing debugging.

- We created a fast preprocessor code for stateless firewalls. This setup allows mimicry of conventional firewall setup, where known stateless information can be used to minimize unnecessary loading of states in the stateful firewall.
- We developed a translating code for porting rules in Juniper NetScreen language to Linux iptables language. This allows us to run and compare our stateful firewall against a typical Juniper firewall for correctness and processing rates.

Significance:
This project fits well with the DHS's strategic goal to protect critical infrastructure. This project will address our cyber security needs of reducing vulnerabilities and attacks on our cyber systems that can damage our nation's critical infrastructures.

This project also aligns well with DOE's research integration goal. In particular, the project will integrate applied research to create transformational solutions to our national security needs. The completion of this project will accurately address the effectiveness of using many-core network processors for future high-performance cyber protection systems.

Leveraging Complexity for Unpredictable yet Robust Cyber Systems
154199

Year 1 of 3
Principal Investigator: J. Mayo

Project Purpose:
Attempts to secure computer systems have consumed decades of effort, resulting in little net progress and a continuing flood of successful attacks. This frustrating outcome strongly suggests that finding a solution requires rethinking the problem and addressing the basic reason that defenders currently cannot ensure security. This reason is the inherent complexity of computer systems, made precise by theorems that no general algorithms exist for answering questions about the behavior of an arbitrary program. Although engineers try to implement intended behaviors and no others, the theorems imply that unintended behaviors, including vulnerabilities, are generically present. Thus, complexity currently gives attackers an asymmetric advantage by affording them a rich environment to exploit vulnerabilities while making protection an effectively unsolvable task.

We are investigating methods for leveraging complexity against attackers so that their task becomes effectively unsolvable, reversing today's asymmetry. We will develop designs, based on diversity and redundancy, for systems that perform their intended function reliably but present a "moving target" to frustrate attackers. Enabling research will focus on automated code transformation, genetic programming, and ways of supporting diversity in compilers, runtime environments, and microelectronics. Our approach aims at generating unpredictability sufficient to thwart entire classes of attacks that rely on implementation incidentals. The strategy applies equally to hardware, software, and the boundaries between them. If successful, our work has the potential to alter the balance of power in cyber security and restore control to system owners.

Summary of Accomplishments:
In our work to date, we explored and evaluated ways of generating program diversity — gaining insight from idealized examples and examining tools applicable to more realistic systems.

We developed an initial categorization of diversity subspaces in cyber systems based on semantic levels. These levels include CPU (central processing unit) microarchitecture, instruction set architecture, firmware/BIOS (basic input/output system), boot loader, operating system, virtual machine, and application, each with its own randomization possibilities. Information gathering on hardware aspects suggested several technologies pertinent to diversity in microelectronics, including maskless lithography, antifuses, and physical unclonable functions.

We identified and evaluated approaches for code transformation and genetic programming. As code examples with a tractable specification but realistic features of combinatorial complexity, we considered programs that play tic-tac-toe and programs that recognize bit strings. We evaluated the effectiveness of diversity generation approaches using these examples, with the goal of generalizing to other cases. We performed genetic programming on Boolean networks (a flexible representation of digital logic, directly related to microelectronics) as an objective way of generating diverse programs from training data.

The genetic programming framework and concepts we developed provided insight on complementary security techniques such as formal methods and fuzzing. We also gained familiarity with existing tools such as Pyevolve (a Python genetic algorithm framework), ROSE (a framework for C/C++ program analysis and transformation), and Coccinelle (a tool for semantic patching of C code) that may help apply our techniques more pragmatically.

Significance:
If successful, this research will contribute important advances in modeling and design of cyber systems, enabling quantifiable security improvements with relevance across the national security mission spaces. Depending on the cost and difficulty of implementation, the techniques developed may be most applicable to systems requiring very high assurance, such as command-and-control systems, mobile autonomous robotic combat systems, and physical intrusion sensing systems.

Via generating large ensembles of implementations of a given functionality, work to date has already enabled more concrete and objective (rather than anecdotal) demonstrations of cyber security risks and mitigations for high-consequence systems of interest to Sandia.

Massive-Scale Graph Analysis on Advanced Many-Core Architectures
154200

Year 1 of 2
Principal Investigator: M. N. Lemaster

Project Purpose:
Cyber security is a field plagued by "information overload." Major breakthroughs will require analysts to develop an intuition for massive datasets, empowering them to experiment with unconventional analysis ideas and reduce massive datasets to a set of indicators that a human can absorb and interpret. This will require high-performance analysis tools that can operate at massive data scales. Graph analysis has the potential to be an extremely powerful tool toward this end and has been shown effective in areas such as malware detection and network flow analysis.

Although well suited for massive-scale graph analysis, architectures like the Cray extreme multi-threading (XMT) are so expensive that only a handful exists. In contrast, many-core systems are affordable enough to be deployed in the field, enabling in situ data reduction. This could change the face of cyber security, particularly in situations when data cannot be securely transported to a central processing location.

This project is primarily aimed at understanding whether many-core architectures can be effectively used to tackle the massive-scale cyber data problem. Toward this end, we will identify the regimes in which a many-core system offers adequate performance and scalability for specific graph analysis tasks and then develop software optimized for these tasks, leveraging Sandia's expertise in graph analysis and multithreaded programming.

The challenge will be achieving high performance on a many-core system. Due to the deep memory hierarchy of many-core architectures, the compiler must make reasonable predictions about memory access patterns. Because the memory access patterns of graph algorithms are so difficult to predict, we will have to craft our algorithms carefully. Our findings could influence the next generation of many-core designs, improving their viability for this application area in the future.

Secondarily, we will identify specific operational cyber security concerns that can be addressed using massive-scale graph analysis techniques. Where feasible, we will develop novel analyses and apply them to real cyber data.

Summary of Accomplishments:
Our primary objective was to evaluate the performance of many-core architectures for massive-scale graph analysis tasks. Toward this end, we designed and tested many possible implementations of an integer hashing algorithm, upon which more advanced graph algorithms can be built, in order to determine the most scalable solution for non-uniform memory access or non-uniform memory architecture (cc-NUMA). We demonstrated that a 32-core SGI Altix UV 10 machine can outperform a 128-processor Cray XMT at only a fraction of the cost. However, we found the XMT to be the more scalable of the two. We also developed and analyzed many implementations of breadth-first search and single-source shortest path algorithms, which we plan to publish in the near future.

Using what we have learned about graph analysis on many-core architectures, we also transformed a graph analysis infrastructure originally designed for the Cray XMT into a multi-platform tool. Because the tool allows easy prototyping of parallel analyses without parallel programming experience, cyber subject-matter experts could use it to experiment with new ideas on full-scale data. This would allow them to more fully understand the characteristics of their data in order to develop a baseline for normal vs. anomalous behavior.

Toward our secondary objective, we developed an analysis of a distributed data exfiltration attack. The analysis takes into account the realities of our data collection capabilities and can be used to put bounds on how much data could have been exfiltrated in a given period of time by an attacker with limited resources. Additionally, it provides insights into the effectiveness of various mitigation strategies.

We also have several other efforts in progress. We are exploring scalable implementations of triangle-finding, subgraph isomorphism, and tensor decomposition algorithms for many-core architectures.

Significance:
The size and affordability of many-core systems makes them ideal for performing in situ analysis, allowing cyber data to be processed in situations where the data cannot be transported due to legal, technological, or operational security restrictions. However, many-core systems can also be used at a central location to synthesize data collected from distributed data sources.

Either of these models is potentially of interest for national security missions, provided that many-core architectures deliver sufficient computational power. Our results have shown that they do deliver comparable performance to bulkier, more expensive systems like the Cray XMT for properly optimized code. We are publishing our algorithms and findings so that they will be available to interested agencies.

Refereed Communications:
E.L. Goodman, M.N. Lemaster, and E. Jimenez, “Scalable Hashing on Shared Memory Supercomputers,” to be published in the proceedings of *Supercomputing 2011*.

Proactive Defense for Evolving Cyber Threats
154274

Year 1 of 2
Principal Investigator: R. Colbaugh

Project Purpose:
There is great interest in developing proactive methods of cyber defense, in which future attack strategies are anticipated, and these insights are incorporated into defense designs; however, little has been done to place this ambitious objective on a sound scientific foundation. Indeed, even fundamental issues associated with how the "arms race" between attackers and defenders actually leads to predictability in attacker activity, or how to effectively and scalably detect this predictability in the relational/temporal data streams generated by attacker/defender adaptation, have not been resolved. This project is addressing these challenges.

We are attempting to characterize the predictability of attacker/defender co-evolution and leverage our findings to create a framework for designing proactive defenses for large (organizational) networks. More specifically, the project will apply rigorous predictability based analytics to two central and complementary aspects of the network defense problem — attack strategies of the adversaries and vulnerabilities of the defenders' systems — and use the results to develop a scientifically grounded, practically implementable methodology for designing proactive cyber defense systems. Briefly, predictive analysis of attack strategies will involve first conducting predictability assessments to characterize attacker adaptation patterns in given domains, and then using these patterns to "train" adaptive defense systems that are capable of providing robust performance against both current and future threats.

The problem of identifying and prioritizing defender system vulnerabilities will be addressed using statistical and machine learning to analyze a broad range of data (e.g., cyber, social media) on recently detected system vulnerabilities, in order to "learn" classifiers that predict how likely it is that new vulnerabilities will be exploited and how soon that exploitation might occur. Two cyber threat case studies will be developed and investigated throughout the project, one selected from the cyber security research community and one that is more comprehensive and of higher priority to Sandia and to external national security partners.

Summary of Accomplishments:
Predictive Analysis —Attacks: Phase One

- Developed new bipartite graph-based approach to transfer learning which outperforms existing methods for network intrusion detection on standard datasets
- Published results in 2011 IEEE ISI (received Best Paper nomination)

Predictive Analysis — Attacks: Phase Two

- Initiated development of hybrid dynamical system approach to generating "synthetic" attack data for use in training defense systems, enabling effective defense against current and near-future attacks
- Demonstrated approach for Spam filtering
- Published results in 2011 *Institute of Electrical and Electronics Engineers (IEEE) Intelligence and Security Informatics*

Predictive Analysis — Vulnerabilities: Phase One

- Demonstrated capability to mine public vulnerability databases (e.g., open source vulnerability database [OSVDB]) and accurately predict the likelihood that given vulnerability will be exploited within specified time-horizon

Predictive Analysis — Vulnerabilities: Phase Two

- Developed new approach to integrating/analyzing cyber data (border gateway protocol [BGP] traffic) and blog data to provide effective cyber early warning
- Collected cyber and blog data associated with several instances of three classes of events: attacks (e.g., denial-of-service [DoS]), natural disturbances (e.g., earthquakes), and quiet periods. Demonstrated method's effectiveness for early warning for DoS events.
- Presented results at 2011 NSA (National Security Agency) Threat Operations Center Extreme Cyber Conference

Methodology for Proactive Defense System Design: Phase One

Specify and document all procedures for training/implementing proactive defense systems (e.g., machine learning algorithms) and performing social media analytics

Case Study One: Proactive Defense Using Public Data

Designed study, collected data, and are currently completing analysis

Case Study Two: Proactive Defense Using Sandia Data

- Identified short list of threats of interest, obtained access to relevant data sources, and initiated characterization of data using predictability assessment methodology
- Initiated development of approach to proactive defense for email threats (e.g., by combining analysis of email dynamics and website browsing activity)

Significance:

Developing robust, proactive cyber-defense methods has the potential to directly and significantly benefit DOE, given that the security of DOE computer networks is a crucial concern. Additionally, the differentiating capabilities to be created in this project are expected to be of importance to DOE's national security partners, for instance in the Intelligence Community, DoD, and Homeland Security, and in the commercial sector. More broadly, similar problems involving anticipation of adversary behavior in evolving attacker-defender settings arise in counterterrorism, counterproliferation, counterintelligence, fraud detection, and financial system security; methods for designing proactive defenses would represent an important contribution in these areas.

Refereed Communications:

R. Colbaugh and K. Glass, "Detecting Emerging Topics and Trends via Predictive Analysis of 'Meme' Dynamics," in *Proceedings of the 2011 AAAI Spring Symposium Series,* March 2011.

R. Colbaugh, "Predictability of Social Dynamics: An Appraisal," in *Proceedings of the 2011 SIAM Conference on Dynamical Systems,* May 2011.

M. Planck, K. Glass, I. Lyman, and R. Colbaugh, "A Framework for Near Real-Time Event Characterization within the Internet," in *Proceedings of the IEEE International Workshop on Network Science,* June 2011.

R. Colbaugh and K. Glass, "Proactive Defense for Evolving Cyber Threats," in *Proceedings of the IEEE International Conference on Intelligence and Security Informatics,* July 2011.

R. Colbaugh and K. Glass, "Agile Sentiment Analysis of Social Media Content for Security Informatics Applications," in *Proceedings of the IEEE EISI Conference*, September 2011.

K. Glass and R. Colbaugh, "Web Analytics for Security Informatics," in *Proceedings of the IEEE EISI Conference,* September 2011.

K. Glass and R. Colbaugh, "Estimating the Sentiment of Social Media Content for Security Informatics Applications," to be published in *Security Informatics*.

R. Colbaugh and K. Glass, "Exploiting Meso-Scale Social Network Dynamics for Predictive Analysis," to be published in *Security Informatic*s.

R. Colbaugh and K. Glass, "Proactive Cyber Defense," chapter to be published in *Springer Integrated Series on Intelligent Systems,* 2012.

Partial Memory Image Analysis
154275

Year 1 of 1
Principal Investigator: S. A. Mulder

Project Purpose:
Traditional approaches to malware analysis involve analyzing binary images as they exist on a disk or travel across a network. Attacks involving code-injection using buffer overflows or related techniques, as well as recent advances in malware such as return-oriented programming, may have substantial capability and never exist on disk. In addition, sophisticated malware may appear dramatically different in memory than observation of a file on disk may allow. We will apply techniques that we have developed for analyzing file images and network captured images to partial memory images. These include characterization, creation of signatures, and correlation with other recognized executable content.

By bringing this information into the Oxide system developed at Sandia, we can leverage the analysis and correlation performed across file-based executable content to characterize and correlate with new sources of executable content. This would extend our current situational awareness capability from the disk and network to memory.

Capturing and recognizing transient states in memory are much more challenging than analyzing files on disk. Techniques such as return oriented programming (ROP) may be extremely time sensitive and any technique that is not robust against partial information will tend to fail. New algorithms to deal with partial matching and time sensitive capture states will need to be developed. These may extend the current research in fuzzy hashing or fuzzy state-machines or new techniques may be needed. Previous related work at Sandia dealing with establishing confidence in disassembly and work with fuzzy hashing techniques are providing a starting point for this investigation.

Summary of Accomplishments:
- We demonstrated an automated process for launching executables into a virtual environment and automatically parsing out the process images.
- We analyzed the differences between processes and executables and built analysis tools to use these differences and similarities
- We demonstrated an automated technique for locating multiple processes generated from the same executable without using metadata such as process name.
- We demonstrated a technique for comparing requested versus actual dynamic-link library (DLL) imports to detect inconsistent behavior.

Significance:
The research expanded our ability to understand the software executing in our environment. It is the first attempt to leverage our abilities in static analysis to detecting new dynamic attack vectors. This directly benefits Sandia's mission in protecting our cyber assets, and more generally, will be applicable to protecting cyber assets across the DOE complex.

Analytic Methodology for Assessing Supply Chains
154352

Year 1 of 1
Principal Investigator: M. C. Foehse

Project Purpose:
We are addressing a binary classification problem: categorizing nodes within a graph as interesting or uninteresting. The principal goal was the development of a classifier which can exploit both labeled data (very expensive) and unlabeled data (inexpensive).

In previous work, we have shown that the community structure of a worldwide web graph possesses considerable predictive power. In this project, we explore a variety of metrics of the web graph's community structure, assessing each metric's utility by evaluating its predictive power for the task of distinguishing interesting and uninteresting graph nodes.

We wish to evaluate three community-finding approaches: Walktrap, wCNM (wireless communications, networking, and mobile computing) and Link Communities. The first two approaches use a graph's nodes as the basis for determining community membership while the Link Communities algorithm uses a graph's links. Once communities are determined, we can use the graph and community metrics to identify interesting graph characteristics, for example, average degree, diameter, clustering coefficient, average path length, and others.

Once we have determined our graph and community metrics, we will use them as inputs to multiple machine learning techniques. Our goal here is to identify which techniques best map the graph and community metrics to a binary classification model. We will examine supervised, semi-supervised and unsupervised techniques.

Summary of Accomplishments:
We built graphs from crawls of the Web and then applied the three community finding approaches: Walktrap, wCNM, and Link Communities. Two of the approaches — Walktrap and wCNM — successfully identified graph communities and allowed us to compute graph and community metrics. We were unsuccessful in the application of the Link Communities algorithm; it was not at all definitive in the identification of communities.

We investigated 33 supervised machine learning techniques using Sandia's Cognitive Foundry and identified the best techniques in the set, those being the perceptron-like learners: MIRA (margin infused relaxed algorithm), relaxed online maximum margin algorithm (ROMMA), and AROMA (association rule ontology matching approach).

We next investigated a new, agile semi-supervised machine-learning algorithm. The key contribution in this algorithm is a method for appropriately smoothing the class estimates over a bipartite graph data model. This method proved very successful in allowing the use of unlabeled data while providing accurate classification as compared to Avatar, a supervised machine learning method that utilizes ensembles. This use of unlabeled data is a significant improvement as compared to the time-consuming generation of labeled data typically required by standard learning methods.

Finally, we investigated statistical graph methods. Using this statistical approach, we can make statistical statements regarding the similarity between nodes and also between communities, for example, node X is similar to node Y with 95% credibility.

Significance:
We have demonstrated a classifier that can successfully characterize graph nodes as interesting or uninteresting using graph and community metrics, coupled with a new, agile, semi-supervised machine learning technique. This new semi-supervised method performed better than existing supervised and semi-supervised techniques while using unlabeled training data, a significant step in the construction of such classifiers.

The statistical graph measures demonstrated that simple, unsupervised methods can identify communities and allow anomaly identification.

Community-Based Resistance to Intrusion in Information Technology Systems
154531

Year 1 of 1
Principal Investigator: R. C. Armstrong

Project Purpose:
Present-day cyber defenses fail against new/unknown threats. The root of the problem is the traditional use of networked commodity computing, wherein general-purpose hardware and networks are largely populated with copies of only a few standard configurations of highly popular operating systems and applications. These codes have narrow specifications for what they must do and very specific policies about the unexpected behavior they will not support, leaving a large space of possible attack vectors to be exploited by malware. Furthermore, cyber security is grafted at the system level, and specifications about what malware looks like are based on past experience with malware. Consequently, malware is successful by ensuring that its signature and behavior cannot be easily distinguished as such, exploiting the relatively static, centralized, and well-understood security systems.

Methods of counteracting these weaknesses include: 1) pervasive security built at all system levels, 2) machine learning for identifying anomalies, combined with reputation systems that restrict the use of resources to “well-behaved” components, and 3) use of cryptographic tags. We are pursuing a strategy in this project based on the idea that these methods can form an integrated solution offering more reliable security by designing computer systems in analogy to biological networks of interacting cells, called “communities.” More specifically, we are pursuing a generic mechanism by which any process can be integrated into a community via a wrapper that supports the classes of interactions that are known in biological communities to generate stable community composition in the face of invading cells or pathogens. Community members will dynamically generate both diverse and shared features, which are difficult for the outsiders to infer. The community will support a distributed machine learning system that leverages cryptographic recognition and reputation auditing as mechanisms to detect and starve cyber attacks.

Summary of Accomplishments:
Through this work, we developed novel schemes for creating programs that are less likely to be broken into by cyber criminals. By “growing” programs through selection or machine learning, we have developed a method by which any number of differently implemented programs that, nonetheless, perform to the same specification can be created. It is well known that this diversity can foil attackers by denying them certitude in the incidentals of implementation necessary to break in. These techniques can produce very simple programs, in any quantity, that range widely in their implementation. This means that every user can have a different copy of the program, requiring an attacker to develop a different exploit for each instance. This would make the proposition of indiscriminate anonymous wide-ranging malware prohibitively expensive to develop.

These programs are likely limited to expressing very low complexity algorithms, and while machine learning can moderately improve the complexity of problem that this technique can handle, it is likely that all but the simplest task is out of reach by these methods alone. A divide-and-conquer approach suggests itself where a complex program is created from simpler pieces. The human programmer’s job is to divide the task into simple enough pieces so that they can be programmed via machine learning or selection. The programmer’s job is not so much programming anymore but architecting a framework of components that can be automatically programmed. Once this framework is in hand, many different versions can be created and continuously re-created that will make it difficult for the attacker to exploit.

Significance:

The complexity of electronics, software, and intelligent devices in high-reliability systems can cause vulnerabilities to be overlooked, whether the vulnerabilities arise by accident or are deliberately introduced. The preponderance of such systems in our daily use and within infrastructure can allow malicious adversaries to cripple our critical systems. Advancement of the knowledge of how to build systems with scalable self-regulation mechanisms can help the nation to defend against threats to our information technology infrastructure, both for critical Sandia Systems and, more broadly, for all federal civilian and military cyber systems.

Sandia Trusted Model of Computation
154587

Year 1 of 1
Principal Investigator: R. C. Murphy

Project Purpose:
Today, computers are constructed from entirely untrusted components (both hardware and software). There are three key components to trust: isolation (of systems and subsystems from each other), resilience (in the face of faults or erroneous data), and security (in the face of malicious attack). The dominant von Neumann model of computation is silent with regard to all three of these. Further, the provenance of commodity hardware and associated software stacks is almost universally unknown. Combined with an ad hoc systems engineering model, these factors create an insurmountable barrier to the production of a secure computing platform. Consequently, security is relegated to application developers. Trust is a complex, system-level problem, and requires coordinated design at all levels. Inadvertently exposing a weakness or vulnerability in a single component can compromise the security of an entire system. In this project, we will rethink the model of computation — with trust as the primary objective function, rather than performance or energy.

We are categorizing and analyzing known threats such as attacks via buffer overruns, corrupting or hijacking an instruction stream, or denial of service by exploiting unintended coupling between unrelated components. We are using that information as a basis for exploring and evaluating architectural elements and techniques, along with new and different architectures for computation (hardware and software). This work will form the foundation for defining the requirements of trusted computing. This foundation, combined with a trusted chain of production and a rigorous verification and validation capability, will establish a baseline definition of trust. This entails a first-principles rethink of computing from the ground up, incorporating isolation, resilience, and security as first-class drivers along with performance and low power. Architecture and design tradeoffs will be influenced in fundamentally new ways, ultimately providing application designers with a much larger and more robust solution space. We will establish laboratory leadership in trusted computing systems.

Summary of Accomplishments:
We created a list of categorized threats and produced corresponding requirements to effectively mitigate them. The categories include key management, system management, integrity checks, and instruction streams. Additional categories specific to each proposed architecture are also included. Each architecture is evaluated with regards to the threats and given a relative mitigation factor (high, medium, low, or none). Although the architectures are still conceptual, if the requirements are met during the implementation, the mitigation should be effective. This methodology of providing threat analysis at the conceptual level with requirements to adhere to during implementation will incorporate principles of trust from the beginning rather than as an attempted after-thought.

We designed the Authenticating Cache architecture to provide instruction stream integrity and authentication from the output of the compiler until the stream is loaded into the cache. Furthermore, the architecture strives to provide similar performance to a typical cache by introducing prediction as a mechanism to compensate for the latency associated with integrity and authentication verifications. We also documented various trade-offs for further enhancing trust and performance within the architecture.

We introduced the notion of a dual compile strategy for parallel heterogeneous execution. One instruction stream is compiled in the typical fashion for a compute engine while the other instruction stream is compiled for a monitor and check engine. We have identified potential trust improvements from the application source code through the execution of that application. We have developed a concept to feasibly verify intended operation during execution.

Significance:
Today, the US is extremely reliant on commercial technologies to provide computing functions for many high-consequence and national security critical functions. The development and manufacture of these technologies has moved to foreign sources, decreasing our confidence in the integrity of these products. Yet, our dependence on them is growing. Trusted computing technologies are an essential component for nuclear security, cyber security, and energy security. This research aids in design of systems that can provide the trusted foundation for all three areas.

Uncertainty Quantification and Substantiation for Machine Learning in the Context of Cyber Security
154815

Year 1 of 3
Principal Investigator: M. A. Munson

Project Purpose:
Cyber security is critically important in safeguarding the networks that support our national interests. Malware and targeted cyber intrusions constantly threaten to disable major systems, exfiltrate sensitive information, etc. Not only must Sandia protect its own networks, but Sandia is playing an increasingly larger role in cyber security as it relates to DOE's core nuclear weapons mission and the critical national security missions of other government agencies.

Detecting malware and other cyber threats is difficult due to the massive volume of data. Machine learning has the potential to detect these threats, but it is not widely used because it functions as a black box. The goal of this project is to make machine learning more usable to analysts by quantifying the uncertainty associated with events of interest. Further, this research will add the ability to reach back into the original data to substantiate detected threats with examples of similar past events. This research will lay the groundwork for tools that reduce information overload by allowing analysts to: 1) prioritize data by both threat level and confidence interval and 2) quickly verify the machine learning output with historical data.

Little research effort has been invested into quantifying the uncertainty in machine learning results and substantiating black box outputs because average-case accuracy and reliability is sufficient for most industrial and academic applications. Stronger guarantees are required for cyber security and other domains of interest. Our approach is to develop three diagnostic capabilities: output confidence intervals, extrapolation detection, and result substantiation.

Summary of Accomplishments:
In FY 2011, we studied how to derive confidence intervals for predictions made by a decision tree, a type of predictive model. (A predictive model predicts an output based on a set of input variables. Machine learning methods construct such models from data.) Ensemble models combine the predictions from multiple decision tree models to form the ensemble's prediction.

- First, we reviewed the literature related to uncertainty in decision tree models and implemented the sole existing technique for deriving confidence intervals for a single decision tree. This baseline method was both too slow for practical use and generated overly wide intervals. We have developed a more practical baseline and anticipate evaluating one additional simple method in FY 2012.
- Second, we created a synthetic benchmark dataset for testing the validity of confidence intervals. The test is designed to check if intervals accurately quantify uncertainty from small sample sizes and uncertainty of model structure.
- Third, we worked with an intern from Sandia's Center for Cyber Defenders to build a portable document format (PDF) parser for extracting indicators of embedded malware in PDF files. This parser will be used to build a data set which will, in turn, be used for assessing how useful confidence information is for analysts prioritizing their efforts.
- Fourth, we designed and tested a novel confidence interval method based on Bayesian decision tree learning. The new method is efficient and produces somewhat more accurate intervals than the baseline method. Unfortunately, the intervals only enclose the true value 65-75% of the time — far

below the specified 90% confidence level. Thus, we learned this approach is insufficient, and other approaches will need to be explored.

Significance:
We now have the benchmarks and methodology for measuring progress on the confidence interval problem. The current confidence intervals are, unfortunately, not accurate enough to be used in Sandia's mission areas. Additional research next year will hopefully lead to better intervals. Accurate confidence information will support cyber security analysts and improve their efficiency through better triaging and prioritization.

The PDF parser opens new possibilities for improved network monitoring. Because it is derived from a PDF viewer, it is able to bypass complex malware obfuscation techniques. This is an important step forward in analyzing and eventually blocking PDF malware throughout the DOE complex.

Peering Through the Haze: Privacy and Monitoring in the Cloud Computing Paradigm
156435

Year 1 of 3
Principal Investigator: D. J. Zage

Project Purpose:
Cloud computing is becoming the infrastructure of choice for hosting data and software solutions for many organizations, necessitating research to understand the vulnerabilities of this paradigm. While some security risks — such as the vulnerability of data during transport — are obvious, the infrastructure introduces new non-obvious threats, particularly those due to the lack of control of the physical hardware. These threats pose significant risks to the integrity of data and user privacy during both data storage and data usage. For example, an untrustworthy cloud service provider has access to all of an organization's data stored on the cloud and it can monitor device usage to further learn about a user. Although some of these risks can be mitigated by leveraging solutions from current research (e.g., cryptographic techniques), creating solutions that maintain the performance and utility of cloud computing while preserving privacy and data integrity remains a challenge. Mitigating these risks is essential for organizations working with sensitive data as failure to do so can result in the compromise of information. This can lead to fiscal loss, embarrassment, and in the loss of critical data.

With the increasing push in governmental sectors towards cloud computing solutions, research is needed to create solutions that maintain data and user integrity even when considering malicious actors. We are attempting to develop a methodology to enable cloud users to store, access, and compute across sensitive data while maintaining security and privacy in terms of the data stored at the provider and in relation to a user's service usage. Our approach will exploit advances in cryptography and communication protocols along with novel uses of the cloud infrastructure to create secure solutions. Additionally, this research will bring us closer to understanding the cloud-computing paradigm in general and further Sandia's leadership in understanding technology critical to the nation.

Summary of Accomplishments:
We have conducted a detailed literature review of relevant topics in secure cloud computing including advances in secure cloud storage, search techniques, user authentication and access control, and cryptography. This has allowed us to identify the strengths and weaknesses of different protocols and come to the general conclusion that many of the protocols are theoretically possible but impractical in practice. Not only will this information be leveraged during future research and the construction of future protocols, we will summarize it in an overview submitted to the Institute of Electrical and Electronics Engineers (IEEE) Security and Privacy magazine (at the urging of an editorial board member), helping to further recognition of Sandia's leadership in critical technological domains. We have also become familiar with current virtualization techniques and have begun to work with other lab members to construct a viable cloud computing testbed. We have begun the formulation of a lightweight protocol which will allow an end-user to store data, being able to independently verify, with high probability, the correctness of both the storage and retrieval of the data.

Significance:
Multiple government agencies stand to benefit from this work as they move data and services to a cloud-computing environment. DOE, DoD, and the Defense Information Systems Agency all espouse the use of the cloud computing as well as utilize cloud computing internally. In a broad sense, any agency needing to provide or use cloud computing while maintaining data integrity and privacy stands

to benefit. While no approach can provide an absolute guarantee of user and data privacy, the economic and social impact of not addressing these issues is potentially staggering.

Secure and Efficient Privacy Preserving Program Obfuscation with Oblivious RAM 156436

Year 1 of 3
Principal Investigator: J. H. Solis

Project Purpose:
Program obfuscation is a software protection technique that attempts to hide internal instructions or operations from unauthorized observers. However, no existing obfuscator is capable of preventing a dedicated and patient adversary from decompiling and reverse-engineering obfuscated code. All software, from trivial applications to critical infrastructures, is defenseless against a determined adversary.

The ideal obfuscator would transform a program into a "virtual black box" that, when executed, leaks no information about the underlying program instructions. Unfortunately, general program obfuscation, in the virtual black box sense, is theoretically impossible. Despite this, alternate obfuscation models have been proposed to investigate scenarios where secure program obfuscation might still be possible. One promising model led to the development of CodeSeal — a provably secure code obfuscation technology. Unfortunately, due to certain restraints, it is primarily limited to small and trivial programs. Extending its capabilities would enable large and complex programs to run securely in untrusted environments while simultaneously preserving program integrity from malicious tampering.

While the current version of CodeSeal is a powerful cryptographic primitive, it only represents the first steps toward a general solution. Due to certain assumptions in the original model, communication overhead limits CodeSeal applicability to small and lightweight programs. We will investigate alternate methods that improve overhead and extend general applicability while still preserving cryptographic security and integrity. For example, private information retrieval and oblivious transfer schemes could retrieve program instructions in a secure and private way. In addition, framing the problem under an oblivious random access machine (RAM) model could securely hide memory access patterns from an adversary. The end result would be a new cryptographically secure, communication efficient, privacy preserving program obfuscation scheme.

Summary of Accomplishments:
We began by applying an oblivious RAM model to CodeSeal and attempted to improve performance bounds by increasing the trusted memory available. Unfortunately, we soon learned that the oblivious RAM transformations we employed were independent of trusted memory size and achieved a poly-logarithmic slowdown in the running time. Instead, we investigated emerging security primitive, physical unclonable functions (PUFs), and its implications on the software protection problem.

The first result is a theoretical analysis showing that traditional non-computational (black-box) PUFs cannot solve the software protection problem against (strong) real world adversaries. We present schemes secure against weak adversaries and present a protection scheme secure against strong adversaries based on trusted hardware.

The second result follows from the result of the first paper and argues that intrinsic PUFs are needed to solve the software protection problem because they are intrinsically involved in processing the information that is to be protected. We describe how sources of randomness in any computing device can be used for creating intrinsic-personal-PUFs (IP-PUF) and present experimental results in using standard commercial off-the-shelf computers as IP-PUFs.

The third result is an initial x86 based implementation of the CodeSeal algorithms. We are currently implementing the Gentry-Razman constant private information retrieval scheme to improve communication overhead (since an oblivious RAM runtime improvement would be small [from poly-log to log]). We hope to finish the implementation shortly and compare benchmarks from both approaches.

Significance:

The relevance of this project to national security missions is the development of techniques that increase the resiliency of the current cyber environment. Developing tools that cryptographically protect sensitive operations from malicious tampering can be used to protect the critical infrastructures on which we all depend. The advancement of these techniques is critical across all areas of cyber space.

Advanced Malware Analytics
157168

Year 1 of 2
Principal Investigator: K. Chiang

Project Purpose:
The malware problem is difficult to solve in today's complex, connected environment where system vulnerabilities are inherent. Malware authors will continue to take advantage of system vulnerabilities as well as human vulnerabilities. Antivirus (AV) and personal security software is abundant (currently 40 companies offer AV solutions), but serve only a best effort at protecting systems and networks. An important strategy to help level the playing field in favor of the defenders is to increase the probability of attribution of bad behavior of an adversary. The forensic analysis repository for malware (FARM) is a Sandia-developed environment used by network defenders on a daily basis for malware analysis, triage, and threat awareness. FARM automates multiple analysis tools commercial-off-the shelf (COTS) and government-off-the-shelf (GOTS) to provide incident response analysts with specific details regarding specific malware samples so that they can make more informed decisions about attack software. Although the FARM framework provides a good starting point for defenders to better analyze attack software, more sophisticated adversaries can tailor their malware to thwart analysis techniques making the job of the defender more difficult. As malware authors develop new tools and techniques for their attack software (malware), the defenders need a way to learn these techniques and ways around them to better analyze the malware. This project identifies three innovative areas of research that will give the defenders new advantages.

Summary of Accomplishments:
- We developed automation to augment the dynamic analysis environment with simulated "user" activity to help analyze malware whose behavior may be user-dependent.
- We developed capability to analyze version-dependent exploitations on popular software like Adobe Reader, browsers, and media plug-ins like Flash.
- We investigated and identified techniques for doing function-level matching for correlating malware.
- We laid the groundwork for hypervisor-based library tracing and parameter extraction to provide a new dimension of malware analysis in the FARM framework.
- We identified potential collaborators at various DoD and government agencies.

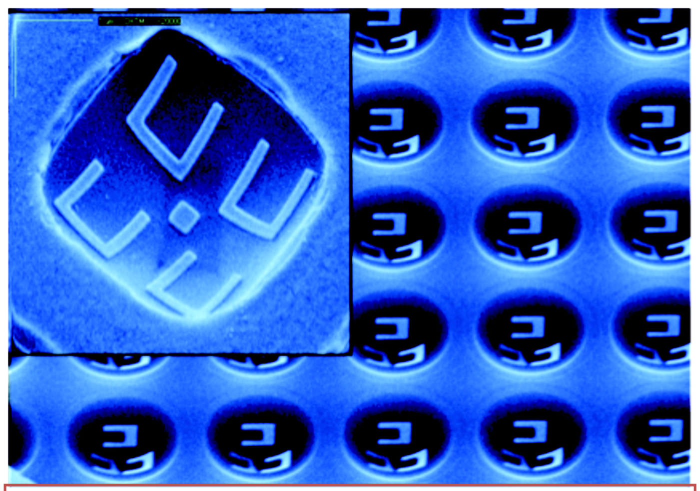
Significance:
An important strategy in defending the nation's computing infrastructure is to increase the probability of attack attribution. The research in this project has enhanced incident-response capability by advancing the state-of-the-art for malicious software research toward this goal. This research will benefit the national security missions of DOE as well as other government agencies in protecting their information infrastructure.

GRAND CHALLENGES INVESTMENT AREA

Grand Challenge projects are designed to address scientific challenges and urgent national security issues that are broad in scope and potentially game-changing in their impact. As such, these projects require the assembly of often large, always interdisciplinary teams of scientists and engineers, and are commonly funded at an annual level of from $1M–$5M. Examples come from areas such as quantum computing, sensor architectures for moment-to-moment surveillance of the environment, nanoscience applications in high-power laser technologies, advanced biological threat detection, and computational approaches to electrical grid reconfiguration to accommodate renewable energy sources.

Metamaterial Science and Technology
Project 131302

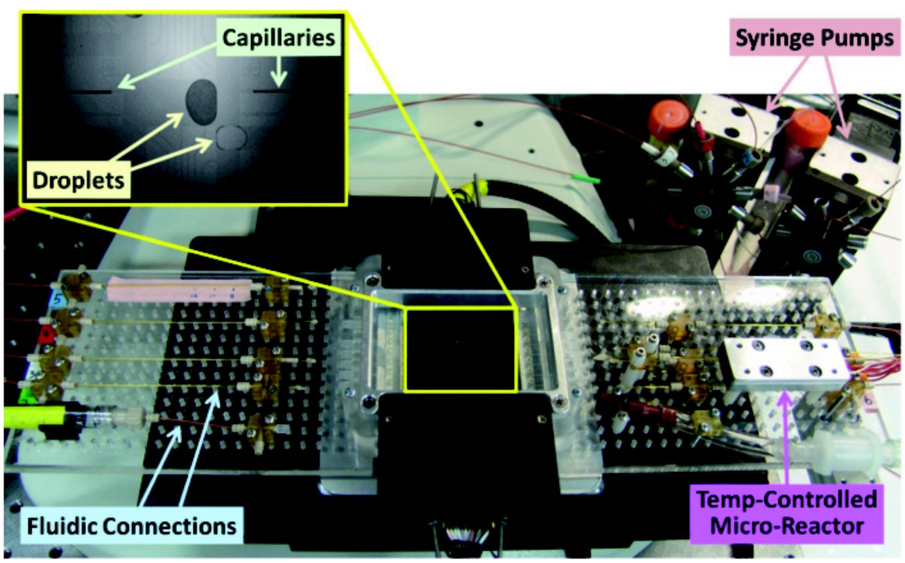
Metamaterials form a new class of artificial electromagnetic materials that provides a device designer with the ability to manipulate the flow of electromagnetic (EM) energy in ways that are not achievable with naturally occurring materials. Artificially structured materials not found in nature, metamaterials represent a new frontier in materials science, in the sense that materials can be designed and created — through micro- and nanofabrication — with particular performance purposes in mind. To operate in this novel realm requires integration of many functionalities, from design and simulation, to synthesis, fabrication, and characterization. This project is conducting just such ground-breaking research, with particular emphasis on materials that are nanostructured to respond to specific electromagnetic (EM) frequencies, providing the ability to manipulate the flow of EM energy in ways not achievable with naturally occurring materials. The project is specifically seeking to manipulate long-wavelength infrared (LWIR) in a low-loss fashion. Although metal metamaterials have been constructed with resonances to radio waves and microwaves, designers and engineers have been unsuccessful in the higher-frequency infrared and visible regions of the EM spectrum because metals show high losses at these frequencies. Therefore, this project is developing new fabrication processes as well as new methodologies to analyze its fabricated metamaterials. A novel nanofabrication technique has been developed, known as "membrane projection lithography," one that is capable of producing 3-D resonator metamaterials with dimensions 100-times smaller than prior fabrication methods.



Colorized scanning electron micrographs of newly fabricated three-dimensional metamaterials in the so-called split-ring resonator configuration.

RapTOR: Rapid Threat Organism Recognition
Project 142042

Amid concern about bioterrorism threats to national security, there is, in addition to the need for rapid diagnostics for *known* biothreat agents, another requirement to detect, identify, and characterize *unknown* biological threats—that is, pathogenic microorganisms not previously encountered and possibly genetically engineered to increase threat and avoid detection. The technique of Next Generation Sequencing (NGS) enables analysis of such unknown pathogens at the genetic (DNA or RNA sequence) level, but only if a suitable sample of the pathogen's nucleic acids (DNA or RNA) is available. This is usually not the case in clinical specimens from infected patients, because the pathogen's nucleic acids exist against the far more abundant and complex background of host (human) nucleic acids. Further compounding the problem is the fact that most clinical specimens are "contaminated" with nucleic acids derived from nonpathogenic microorganisms that live in symbiotic relationships with humans, the "human microbiome." Thus, when clinical samples are analyzed using a "brute-force NGS" approach (sequencing the entire collection of nucleic acids recovered from a patient sample, for example), the vast majority of DNA and RNA sequences (genetic information) are uninformative, because most belong to either human cells or to the human microbiome, with vanishingly few deriving from the nucleic acids of either known or genetically altered or unknown pathogens. This "needle in a haystack" problem boils down to wasted time and resources, making it highly unlikely that a pathogen's nucleic acids will be discovered quickly—in time to characterize the nature and biological activity of the pathogen in causing morbidity and mortality in human populations. The goal of this project is to develop and demonstrate new strategies, methods, and technologies for time- and cost-efficient use of NGS for characterization of known and unknown pathogens in clinical samples. To this end, RapTOR is developing a microfluidics-based automated molecular biology (AMB) platform that enables rapid and selective purification, amplification, and formatting of pathogen-derived nucleic acids for NGS analysis. In general, the strategy is to deplete nucleic acids of human origin, and those derived from the human microbiome. Accomplishing this will, in effect, magnify any other nucleic acids in a sample collected from a person — that is, those of any pathogenic microorganism that might be present.



Overview photo of RapTOR automated molecular biology platform.

Grand Challenges Investment Area

Metamaterial Science and Technology
131302

Year 3 of 3
Principal Investigator: M. B. Sinclair

Project Purpose:
Metamaterials form a new class of artificial electromagnetic materials that provides a device designer with the ability to manipulate the flow of electromagnetic (EM) energy in ways that are not achievable with naturally occurring materials. Indeed, recent theoretical investigations have revealed several astonishing applications, ranging from electromagnetic cloaking to subdiffraction-limited imaging that would become possible if the underlying metamaterials could be developed to a sufficient level. However, in spite of these and other advances in the theory of these new materials, progress toward practical implementation of metamaterials, particularly at infrared and visible frequencies, has been hampered by a combination of optical losses, the narrow band nature of the resonant metamaterial response, and the difficulty in fabricating fully 3D structures. The Metamaterial Science and Technology (MST) project seeks to develop useful metamaterials operating in the Long Wave Infrared (LWIR) spectral region by, 1) reducing the absorptive losses of infrared metamaterials operating in the LWIR (8-12 microns) spectral range to the extent necessary to enable low-loss applications, 2) engineering desired absorption features when necessary for absorptive or emissive devices, and 3) developing designs and fabrication protocols for 3D metamaterials supporting volumetric energy flow and operating at multiple incidence angles and multiple polarizations.

To develop low-loss metamaterials, we must reduce or eliminate the use of lossy metallic resonators that have thus far been the mainstay of metamaterial designs. Thus, we are pursuing new metamaterial approaches, such as the utilization of low-loss dielectric resonators that require the incorporation of new material sets and the development of new fabrication techniques. Such an undertaking can only be successful through a highly coordinated project that intertwines efforts in the areas of theory and modeling, material science, and nano/micro fabrication.

Summary of Accomplishments:
We performed rigorous and quantitative analysis of several metamaterial architectures and demonstrated the following:

1. ohmic losses of metallic metamaterials are too large for metamaterial applications such as lenses that require good transparency;
2. polaritonic materials can be utilized to improve metamaterial performance, most notably by acting as negative permittivity host materials in dielectric resonator-based metamaterials;
3. dielectric resonator-based metamaterials represent the best route to low-loss metamaterials; and,
4. independent tuning of the permittivity and permeability of dielectric resonators can be achieved using a variety of strategies.

We identified the best high dielectric constant materials to utilize for dielectric resonator-based metamaterials, and fabricated and characterized the first-ever all-dielectric infrared metamaterial. We developed a novel fabrication process called membrane projection lithography (MPL) for the production of split ring resonators (SRR)-based metamaterials. MPL enables a 1000-fold reduction in the unit cell dimensions and enables the production of fully 3D, bulk metamaterials in the thermal infrared. We developed a new, fast, efficient, and accurate metamaterial unit cell design methodology called Isolated Particle Simulation and Moments. We developed a "subcell" simulation tool that reduces the computational burden for metamaterial structures such as SRRs by a factor of 1000, thereby enabling the direct numerical simulation of entire metamaterial devices such as prisms or lenses. We utilized Sandia's Red Sky supercomputer to perform full wave simulation of an entire negative refractive index prism consisting of 8000 resonators. We developed group theory analysis to guide the design of metamaterial unit cells. We developed a new low-loss infrared polymer called polynorbornene that combines the attributes of low infrared loss, photopatternability, and chemical crosslinking for mechanical strength. We constructed two complementary characterization tools that allow us to experimentally determine the amplitude and phase of the transmission and reflection coefficients of metamaterial samples.

Significance:

Our new infrared metamaterials may enable new optical devices with increased functionality and lower size, weight, and power (SWaP) in nonproliferation and other national security applications, enabling tunable infrared metamaterials for lightweight and large-aperture variable focus infrared systems, flat camera imagers, adaptive and beam steering optics for directed energy applications, and optical limiter materials for laser threat defeat systems. Efficiencies in solar/thermal power may be enhanced by engineered directional/spectral selective absorbers and emitters. Our progress may enable recent radio frequency cloaking demonstrations to be transferred to the infrared regime. Technology surprise in this area is also lessened.

Refereed Communications:

L.I. Basilio, L.K. Warne, W.L. Langston, W.A. Johnson, and M.B. Sinclair, "A Quick and Easy Simulation Procedure to Aid in Metamaterial Unit-Cell Design," *IEEE Antennas and Wireless Propagation Letters*, vol. 10, p. 1, October 2011.

D.B. Burckel, J.R. Wendt, I. Brener, and M.B. Sinclair, "Dynamic Membrane Projection Lithography," *Optical Materials Express*, vol. 1, pp. 962-969, 2011.

R.D. Rasberry, Y.J. Lee, J.C. Ginn, P.F. Hines, C.L. Arrington, A.E. Sánchez, M.T. Brumbach, P.G. Clem, D.W. Peters, M.B. Sinclair, and S.M. Dirk, "Low Loss Photopatternable Matrix Materials for LWIR-Metamaterial Applications," *Journal of Materials Chemistry*, vol. 21, pp. 13902-13908, June 2011.

J.A. D'Archangel, G.D. Boreman, D.J. Shelton, M.B. Sinclair, and I. Brener, "Releasable Infrared Metamaterials," *Journal of Vacuum Science and Technology B*, vol. 29, p. 051806, September 2011.

A. Gabbay, J. Reno, J.R. Wendt, A. Gin, M.C. Wanke, M.B. Sinclair, E. Shaner, and I. Brener, "Interaction Between Metamaterial Resonators and Intersubband Transitions in Semiconductor Quantum Wells," *Applied Physics Letters*, vol. 98, p. 203103, 2011.

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C.M. Reinke, T.M. De la Mata Luque, M.F. Su, L.I. Basilio, L.K. Warne, M.B. Sinclair, and I. El-Kady, "Group-Theory Approach to Tailored Electromagnetic Properties of Metamaterials: An Inverse-Problem Solution," *Physical Review E*, vol. 83, p. 066603, June 2011.

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Reimagining Liquid Transportation Fuels: Sunshine to Petrol
131303

Year 3 of 3
Principal Investigator: J. E. Miller

Project Purpose:
This project addresses two of the most daunting problems facing humankind in the twenty-first century: energy security and climate change. Our vision for achieving this is captured in one deceptively simple chemical equation:
Solar Energy + xCO_2 + (x+1) H_2O --> C_xH_{2x+2}(liquid fuel) + (1.5x+.5) O_2

This effectively describes the use of solar energy to reverse combustion. It is also representative of the photosynthetic processes responsible for much of life on earth and, as such, summarizes the biomass approach to fuels production. Regrettably, photosynthesis and, consequently, biofuels, have very low sunlight-to-hydrocarbon conversion efficiency and can also suffer other serious shortcomings. Thus, an alternative approach, one not limited by photosynthesis, one that more directly leads to a liquid fuel, is highly desirable. The development of a process that efficiently, cost effectively, and sustainably re-energizes thermodynamically spent feedstocks to create reactive fuel intermediates would be an unparalleled achievement and is the key challenge that must be surmounted to solve the intertwined problems of accelerating energy demand and climate change. We propose that the direct thermochemical conversion of CO_2 and H_2O to CO and H_2, universal building blocks for synthetic fuels, serve as the basis for this process. To realize this concept, we must address and solve the complex chemical, materials science, and engineering problems associated with thermochemical heat engines and the crucial enabling metal-oxide working materials. The programmatic goal of this project is to establish Sandia as a recognized leader in the field of beneficial utilization or recycling of CO_2, and to establish the technical plausibility of this approach to liquid fuels production.

Summary of Accomplishments:
Major accomplishments for the three principal project focus areas are as follows:

Materials:
- Identified key attributes for achieving high efficiency and operability in a thermochemical reactor: these include thermodynamic parameters, materials dimensions, and physical properties.
- Elucidated and convincingly demonstrated the mechanism by which iron oxide is rendered cyclable by zirconia supports and the factors limiting performance.
- Measured kinetic parameters for reduction and oxidation of ferrite and ceria materials for use in reactor modeling.
- Implemented and/or developed and applied thermodynamic models to predict performance and guide future materials efforts.
- Applied state-of-the-art surface science techniques to advance the fundamental science behind the interactions of iron oxides and zirconia surfaces.

Reactors:
- Identified key attributes for achieving high efficiency in a thermochemical reactor. These include continuous on-sun operation, sensible energy recovery (recuperation), minimal work input, pressure separation between reaction chambers, direct solar absorption, chemical and mechanical durability, and inherent reaction product separation.

- Demonstrated key attributes of CR5 (Counter Rotating Ring Receiver Reactor Recuperator) most significantly, continuous production on-sun and inherent product separation.
- Produced a multi-ring, multi-dimension model of the operating CR5 to guide development efforts.
- Demonstrated production of CO from CO_2 at an efficiency of 1.7%.

Systems:
- Developed detailed plant and economic models for solar fuels. Applied these to define optimum designs, but also to define efficiency targets for thermochemical reactors.
- Demonstrated the potential for thermochemistry to be a viable option for fuel production.
- Identified key areas for technology development to improve end-to-end system performance.
- Identified the primary economic drivers behind solar thermochemical fuel cost.

Significance:
Project accomplishments speak directly to the long-term availability and price of transportation fuels; these are closely linked to our economic and national security. This work is consistent with two of the four DOE goals outlined in the 2011 Strategic Plan: Goal 1: Catalyze the timely, material, and efficient transformation of the nation's energy system and secure US leadership in clean energy technologies; and Goal 2: Maintain a vibrant US effort in science and engineering as a cornerstone of our economic prosperity with clear leadership in strategic areas. The work is also consistent with three energy, climate, and infrastructure security (ECIS) National Challenges: 1) reducing dependence on foreign oil, 2) advancing credible carbon management strategies, and 3) strengthening the nation's S&T base to accelerate industry for energy security. The research enhances core laboratory strengths including materials, energy, advanced computing, basic science, engineering science and systems engineering and analysis.

Refereed Communications:
J.R. Scheffe, A.H. McDaniel, E.N. Coker, B.W. Jacobs, M.D. Allendorf, and A.W. Weimer, "Hydrogen Production via Chemical Looping Redox Cycles using Atomic Layer Deposition-Synthesized Iron Oxide and Cobalt Ferrites," *Chemistry of Materials*, vol. 23, pp. 2030-2038, April 2011.

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E.N. Coker, A. Ambrosini, M.A. Rodríguez, and J.E. Miller, "Ferrite-YSZ Composites for Solar Thermochemical Production of Synthetic Fuels: In Operando Characterization of CO_2 Reduction," *Journal of Materials Chemistry*, vol. 21, pp. 10767-10776, 2011.

B. Meredig, A. Thompson, H.A. Hansen, C. Wolverton, and A. van de Walle, "Method for Locating Low-Energy Solutions within DFT+U," *Physical Review B*, vol. 82, p. 195128, November 2010.

E.N. Coker, A. Ambrosini, M.A. Rodriguez, T.J. Garino and J.E. Miller, "Production of Hydrogen and Carbon Monoxide from Water and Carbon Dioxide through Metal Oxide Thermochemical Cycles," American Ceramics Society, *In Materials Challenges in Alternative and Renewable Energy,* G.G. Wicks, J. Simon, R. Zidan, et al., eds., vol. 224, pp. 37-49.

Featureless Tagging Tracking and Locating
131305

Year 3 of 3
Principal Investigator: R. C. Ormesher

Project Purpose:
Tagging, Tracking, and Locating (TTL) people, assets, and materials of high importance are integral to numerous national security and defense missions. Existing TTL systems, including those developed at Sandia, enable these missions within certain constraints. However, they do not provide the entire set of capabilities that are required for many TTL missions. Existing TTL systems necessarily trade between geographic range, persistence, geolocation precision, physical size, or some combination thereof.

This project pursued the development of a featureless tagging, tracking, and locating (FTTL) system that provides broad-area coverage and featureless capabilities. Broad-area coverage provides the ability to cover large geographical regions, continuously 24 hours a day, 7 days a week, and locating with a single reception by the tag interrogator. The featureless capability provides a tag that is extremely difficult to detect, both electronically and physically. The ability to accomplish these goals relies on innovations made in three key technology thrusts including advanced signal processing, microelectromechanical system (MEMS) microresonator delays, and placement-insensitive antennas. We have worked to improve the ability to avoid signal interception and detection. Two new phase processing techniques are beginning to show progress for practical use with small beacon tag sources. Advances in the use of MEMS microresonators to provide waveform storage in a synthetic aperture radar (SAR)-tag mode is also ongoing with recent success at frequencies as high as 13.3 GHz. We also researched the use of placement-insensitive antennas to allow TTL users greater flexibility to use devices for tagging. Technologies emerging from these research thrusts have been combined in a proof-of-concept demonstration illustrating the strengths of a featureless approach including wide-area coarse geolocation by a beacon tag followed by fine geolocation by an integrated SAR-radar tag.

Summary of Accomplishments:
Under this project, we have made several scientific and technical advances that provide a framework and set of tools for enabling such a system.

We created and developed new featureless signaling waveforms, detection and geolocation algorithms, and a novel tag architecture, which result in an innovative dual-mode, broad-area, featureless TTL capability. We made significant technical advances in MEMS acoustic microresonator delay elements, and antenna technologies, which result in a tag device that can be physically very small. We developed a small dual-mode tag and demonstrated this tag with new waveforms, antennas, and processing algorithms on a variety of platforms. As a result of this research, many follow-on projects were funded, numerous patents were filed, and conference presentations were published. The microresonator team was also honored with an R&D100 Award.

Significance:
Terrorism and proliferation of weapons of mass destruction (WMD) have become the central threat to the security of the United States. These threats were addressed in a December 2004 Defense Science Board study entitled "Transition to and from Hostilities."

Development of a TTL system that addresses anti-terror related missions and rogue development and manufacture of WMD requires extending current technology and developing expertise that we do not currently possess. A system having "featureless" elements and useful world-wide coverage will be a critical tool for tracking people, assets and materials, thus allowing our nation to mitigate threats to its national security.

RapTOR: Rapid Threat Organism Recognition
142042

Year 2 of 3
Principal Investigator: T. Lane

Project Purpose:
Dramatic advances in biotechnology make technical surprise due to genetically engineered bioweapons a growing threat to national security. Our nation is blind to such "unknown" biological agents—its biodefense and public health infrastructure is designed to counteract previously characterized ("known") pathogens. Modern approaches to discover and characterize unknown pathogens are slow and labor-intensive, requiring specialized laboratory facilities and expertise. They can also be wholly ineffective in identifying pathogens that are non-culturable or unusual. The Rapid Threat Organism Recognition (RapTOR) project is developing a novel automated molecular biology approach combined with data analysis tools and an informatics architecture to create a new capability based on Ultra High Throughput Sequencing (UHTS) of nucleic acids to detect and characterize unknown bioagents rapidly enough for decision-makers to effectively respond to an attack or outbreak.

The technical challenges include accelerating complex multistep nucleic acid manipulations and re-engineering these processes in an automated and high-throughput architecture; developing the capability to process and understand extremely large datasets associated with UHTS, and answering key questions about human biology, such as the level and diversity of microbial loads and host-response signatures.

Solving the problem of the unknown biological threat requires a paradigm shift in biodetection: we must create the ability to detect unknowns without a priori knowledge of the agent. The key to this shift will be the integration of several technical innovations in molecular biology, microfluidics and bioinformatics that will enable UHTS to obtain maximal genetic information from an unknown pathogen against an otherwise overwhelming host background of nucleic acids. Because of these capabilities, in the event of an attack with an unknown agent, RapTOR has the potential of preventing mass casualties, and also of leading the field in complex nucleic acid manipulation and analysis.

Summary of Accomplishments:

- Developed and standardized customized preparation trains for extraction, amplification, and formatting of DNA and RNA (cDNA) for second-generation sequencing.
- Demonstrated success with clinical samples (blood cells and plasma, nasopharyngeal swabs), enabling characterization of "background" in non-infected samples.
- Developed protocols for normalization-mediated and capture-mediated suppression of human (and concomitant enrichment of pathogen) nucleic acids in clinical samples; demonstrated >10-fold suppression, currently optimizing to improve turnaround time and reproducibility.
- Acquired high-value clinical samples containing unknown pathogens, for forthcoming rigorous test of RapTOR approach.

The automated molecular biology platform development team accomplishments for FY 2011 include the development and subsystem integration of the digital microfluidic hub (DMF) (2011 Society for Laboratory Automation and Screening [SLAS] Innovation Award). With this platform, a magnetic bead DNA clean up assay has been performed (manuscript submitted). Hydroxyapatite separation column has also been successfully tested with the DMF central hub through in-plane capillary interface. Additionally, capillary gel electrophoresis quantitation method has been demonstrated and integrated with DMF droplet platform (multiple conference oral presentations). Hardware for the normalization module and PCR module have been built and readied for DMF integration.

Bioinformatics Core established an automated pipeline for rapid analysis of clinical metagenomic sequence data to identify pathogen species and profile species composition of samples. Implemented on a specialized server infrastructure we created, the pipeline allows for users to track preparation and analysis of complex sample sets through a database and web portal user interface, and carries out rapid comprehensive taxonomic analysis (~ 2 hours per million DNA or RNA reads). We also created a specialized pipeline for quantitative analysis of experiments on sequence background suppression. These pipelines are currently in beta test by biology users.

We have used the metagenomic pipeline to analyze dozens of clinical samples of RNA from nasopharyngeal swabs and human plasma, and supplied reports of pathogen and microbial content.

Significance:

RapTOR will provide Sandia and the nation with a new way to address the serious threat of natural, accidental, or intentional release of unknown biological agents. This is a significant public health and national security problem of interest to a broad array of sponsors and stakeholders, including the Department of Homeland Security Chem/Bio S&T Directorate, the Department of Defense's Transformational Medical Technologies Initiative, and the National Institutes of Health National Institute of Allergy and Infectious Disease. Strategic plans for these organizations call for new or expanded efforts to address emerging and engineered biological agents within the next five years.

Refereed Communications:

H. Kim, M.S. Bartsch, R.F. Renzi, J. He, J.L. Van de Vreugde, M.R. Claudnic, and K.D. Patel, "Automated Digital Microfluidic Sample Preparation for Next Generation DNA Sequencing," *Journal of Laboratory Automation*, vol. 16, pp. 405-414, December 2011.

AQUARIUS: Adiabatic Quantum Architectures in Ultracold Systems
152501

Year 1 of 3
Principal Investigator: A. J. Landahl

Project Purpose:
AQUARIUS' vision is to develop a quantum computing architecture whose resource requirements are more achievable than conventional approaches because of the intrinsic noise immunity offered by adiabaticity. A quantum computer is capable of speeding up the solution to numerous problems in our national interest, including those in simulation, energy, and cyber-security.

To achieve this vision, AQUARIUS' goals are to experimentally demonstrate an adiabatic quantum optimization (AQO) algorithm in two technologies,

1. Neutral atoms trapped in an optical-trap array, and
2. Electron spins trapped in semiconductor nanostructures,

and for these technologies to evaluate the potential for fault-tolerant universal adiabatic quantum computation (AQC) architectures.

The key experimental challenges are characterizing and adiabatically controlling "always-on" qubit interactions and integrating high-fidelity qubit readout. The key theoretical challenges are developing realistic noise models and adapting fault-tolerance concepts from quantum circuit architectures to AQC architectures.

Previous experimental research has predominantly focused on superconducting-qubit technology, which may not be best suited to AQC architectures. Previous theoretical research has predominantly focused on bringing error-correction to AQC instead of AQC to error correction.

AQUARIUS will diversify the AQC technology base and explore new ways of making AQC architectures fault tolerant. This project leverages several unique Sandia capabilities, including the Microsystems and Engineering Sciences and Applications (MESA) fabrication facility (fab), the Center for Integrated Nanotechnology (CINT) fab, and high-performance computing (HPC) facilities.

Most existing quantum computing efforts are pursuing the quantum circuit architecture, in which an algorithm is expressed as a sequence of simple operations. The price for this simplicity is high — each operation must be error free to at least one part in 10,000 to operate fault tolerantly. Unfortunately, most groups are so heavily invested in this approach that it requires an LDRD effort to explore alternatives. An experimentally proven resource reduction and a design path forward for scalable universal fault-tolerant AQC could reshape how quantum computing R&D is approached.

Summary of Accomplishments:
We set up three new laboratories (neutral-atom, atomic-precision lithography, cryo-measurement) and secured major equipment for the latter two (adsorbed phosphine- scanning tunneling microscopy [PH3-STM] system, dilution refrigerator).

In our neutral-atom lab, we created a magneto-optical trap (MOT) of roughly a million Cs atoms at 100 microkelvin. We created an optical dipole trap and demonstrated loading/unloading of single atoms from the MOT. We drove coherent Rabi oscillations in the trapped atom, establishing that we have a controllable qubit. We designed and fabricated diffractive optical elements for two-zone, three-zone, and bottle-beam traps (world firsts) using our MESA facility. We trapped three individual atoms in our three-zone trap (world first).

In our cryo-measurement lab, we measured the charge and charging energy of double-quantum-dots that we designed and fabricated in our MESA facility, establishing that we can generate a spin-based qubit. We also demonstrated that we could generate a charge-based qubit, which is an easier task, as it does not require single-electron well occupation. We anticipate charge qubits will accelerate our progress.

In our atomic-precision lithography lab, we demonstrated hydrogen passivation of silicon surface monolayers and controllable etching of features down to 0.7 nm. We demonstrated and characterized epitaxial silicon growth to be used in P-donor encapsulation. We designed and fabricated an ultrahigh-vacuum PH3-STM system and secured necessary safety certifications. We performed preliminary investigations on atomic-precision alignment of wire-bonding features on silicon substrates.

Our architecture team developed predictive software simulators for our planned adiabatic processors, including in-house detailed noise models. The simulators have gone beyond simple predictive modeling and have been used to assess hypothetical larger-scale designs incorporating error suppression protocols. We developed new "holonomic" schemes for implementing gates adiabatically in the circuit architecture, but we also showed that holonomic approaches are not generically robust to DC energy-splitting perturbations, which we expect to be common.

Significance:
"Quantum information science has the potential to expand and strengthen the US economy and security in the 21st century just as transistors and lasers did in the 20th century" (White House Office of Science and Technology Policy, "A Federal Vision for Quantum Information Science," December 2008).

AQUARIUS directly supports US leadership in computer technologies, far beyond tomorrow's high performance computers and exascale computing. Potential applications of interest to Sandia, DOE, and other agencies include the following:

- Detection, image classification, and pattern matching;
- Simulation of complex systems including biological materials, proteins, and pharmaceuticals;
- Optimization of complex systems.

Enabling Secure, Scalable Microgrids with High Penetration Renewables
152503

Year 1 of 3
Principal Investigator: S. F. Glover

Project Purpose:
The electric power grid is evolving to a state that has yet to be defined. Uni-directional power and information flow will be replaced by bi-directional flow as new generation sources distribute throughout the electric grid of the future. Renewable and other distributed energy sources cannot be economically and reliably integrated into the existing grid because it has been optimized over decades for large centralized generation sources. Today's grid model is based on excess generation capacity (largely fossil fuel), static distribution/transmission systems, and essentially open-loop control of power flow between sources and loads. This leaves the grid extremely vulnerable to terrorist attacks, natural disasters, and infrastructure failures. While developing cost-effective and reliable energy systems has been a concern of both the DOE and the DoD in the past, energy surety — providing cost-effective supplies of energy that are reliable, safe, secure and sustainable — has become increasingly important to both agencies. This presents an exceptional opportunity to introduce and validate the transformational concepts presented in this project to impact existing Sandia collaborators in the DoD as well as in the broader national arena.

We are developing a novel intelligent grid architecture, Secure Scalable Microgrid (SSM), based on closed loop controls and an agent-based architecture supporting intelligent power flow control. Unlike some other initiatives, this bold approach will enable self-healing, self-adapting, self-organizing architectures and allow a trade-off between storage in the grid versus information flow to control generation sources, power distribution, and where necessary, loads. Incorporating agent-based distributed nonlinear control to maintain reliable energy distribution while minimizing the need for excessive storage or backup generation will be a key step toward extreme penetration of renewable energy sources. The development of dynamic nonlinear source models, scalable agent-based architectures, and multi-time-variant simulations will be key components to this solution.

Summary of Accomplishments:
The project is on schedule regarding control theory research and advancement with implementation on specific test bed models and hardware awaiting model refinement and hardware construction. The test bed has been modeled, simulated, and will be revised once the hardware is constructed and operational. Hardware for the Sandia's advanced microgrid test bed has been designed and a formal design review was held, with experts from Purdue University, Paul C. Krause and Associates, and Solarbridge Technologies participating. Assembly of the test bed is ahead of schedule.

Construction of the microgrid test bed has already begun with work in progress on the programmable direct current load and the automatically reconfigurable bus, which is the backbone of the microgrid test bed. An invention disclosure has been initiated regarding energy storage emulation. A report has been generated that documents a library of models for stochastic and deterministic sources, converters, inverters, and loads: "Integrated Simulation of Microgrid Component Models", May 21, 2011. Informatics, Hamiltonian, and local control strategies have been simulated in an integrated MatLab-based simulation. Control research has spanned a range of critical problems important to microgrid systems. These include: nonlinear power flow control design for combined conventional and variable generation systems, transient stability and performance based on nonlinear power flow control design of renewable energy systems, control theory associated with optimization functional, optimal power flow with application to renewable energy grid integration, closed loop optimal load control with application to renewable energy grid integration, analysis of Fisher information and Hamiltonian control for microgrids, and schema necessary for high-level informatics based control of microgrids.

This research has resulted in eight conference papers (two invited), one journal paper, a monogram, a book, five invention disclosures, and two patents. Additional publications and advancements are in process.

Significance:
This research and development has the ability to establish Sandia as a world leader in the design of secure scalable microgrids. The focus of this work will be on expanding our capabilities in the secure scalable microgrid mission space within the DoD. This research also has the potential to significantly impact the design of the future US power grid and the evolution of Smart grid technology, which are major DOE Office of Electricity and Energy Efficiency and Renewable Energy missions. This vision will be accomplished through the development of advanced control theories and architectures to enable secure and reliable high penetrations of renewable energy into the power grid. This research is impacting the general S&T community, as follows:

- Delivery of a keynote presentation as one of four invited international control experts at the 2011 Institute of Electrical and Electronic Engineers Control System Society's Multi-Conference on Systems and Control (MSC) in Denver September 28-30, 2011
- Organization of invited sessions on control of power generation systems for the 2011 Institute of Electrical and Electronic Engineers Control System Society's Multi-Conference on Systems and Control (MSC) in Denver September 28-30, 2011
- Organization of a workshop on "Nonlinear Control Design: Hamiltonian Surface Shaping and Power Flow Control Applied to Renewable Energy Systems Scenarios" for the 2011 Institute of Electrical and Electronic Engineers Control System Society's Multi-Conference on Systems and Control (MSC) in Denver September 28-30, 2011
- Leading the kickoff meeting for the newly established Institute of Electrical and Electronic Engineers Control Systems Society Technical Committee on Power Generation
- Participation as a member of the new Institute of Electrical and Electronic Engineers Control System Society's Technical Committee on Smart Grids
- Publication of the book, "Nonlinear Power Flow Control Design: Utilizing Exergy, Entropy, Static and Dynamic Stability, and Lyapunov Analysis"
- Giving a course based on the new book and the work from this project covering the interplay of information theory and control with application to control of energy systems at the University of Padova in Venice, Italy
- Technical reviews for: the Institute of Electrical and Electronic Engineers Control Systems Society, Institute of Electrical and Electronic Engineers Power Electronics and Machines for Wind Applications (PEMWA) conference, Institute of Electrical and Electronic Engineers Transactions on Energy Conversion, Institute of Electrical and Electronic Engineers Transactions on Industrial Electronics, Institute of Electrical and Electronic Engineers Transactions on Smart Grid, and Institute of Electrical and Electronic Engineers Transactions on Sustainable Energy

The Microgrid mission manager is using the secure scalable microgrid grand challenge lab directed research and development concepts to develop new collaborations in networked microgrids. We have just completed the final round of reviews with a proposal to demonstrate networked microgrids at a military base. One of our collaborators is now interested in including networked microgrids in our annual operating proposal with opportunities involving microgrid collectives at Navy bases also being explored.

Refereed Communications:

R.D. Robinett, III and D.G. Wilson, “Power Flow Control for Multibody Systems Utilizing Static and Dynamic Stability and Lyapunov Analysis,” to be published in the *Journal of Intelligent Control and Automation*.

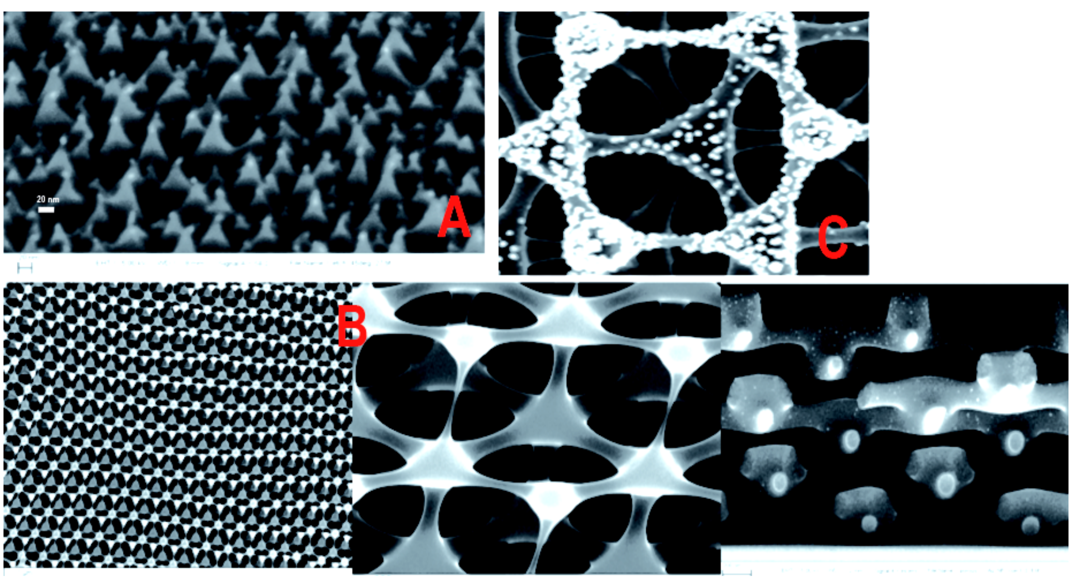
SENIORS' COUNCIL INVESTMENT AREA

This investment area supports a diversity of research projects under the national security umbrella, which are deemed worthy of funding under the auspices of the Seniors' Council, a cadre of Sandia senior scientists. Other than the fact that they tend to be of exceptionally high risk, there is no per se restriction on the topical area of the research proposal, so projects generally fall into several different scientific areas, whose only link is the common thread of the Laboratories' national security mission.

Nanoparticle Modification of Photodefined Nanostructures for Sensor and Energy Applications

Project 148067

This project is exploring the attributes and potential applications of photolithographically definable pyrolyzed photoresist carbon films, creating a diversity of carbon nanostructures with a broad array of potential applications. Beginning with photo-patternable organic resins from commercial photoresist inks, a high-temperature reducing environment transforms them into photopatternable carbon films that can be subsequently modified by maskless interferometric lithography (IL) to form nano- and microstructures, themselves modified through ingenious chemistry. From regular patterns of carbon pyramids each capped by a gold nanoparticle, or 3D porous carbon structures with micro or nanocaverns into which cells, enzymes and nanoparticles can be trapped, or which can be decorated by metal catalysts such a palladium, the potential applications for these structures are numerous. Water purification, filtration and concentration of chemical and/or biological agents, energy storage via batteries or ultracapacitors, fuel cells and hydrogen storage all fall into that realm. For example a proof-of-concept study with palladium-decorated porous carbon structures has demonstrated a significant increase in catalytic activity toward methanol oxidation, demonstrating the microstructure's potential application as a fuel cell anode.



A. Lithographically etched carbon pyramids, each capped by a gold nanoparticle; B. Three views (left, lower magnification, center, higher magnification, right, cross-section) of a 3D porous matrix defined by IL; C. Palladium grown onto the matrix, after seeding with gold nanoparticles.

Seniors' Council Investment Area

Nanoparticle Modification of Photo-defined Nanostructures for Sensor and Energy Applications
148067

Year 2 of 2
Principal Investigator: R. Polsky

Project Purpose:
The purpose of this project is to explore photolithographically definable pyrolyzed photoresist carbon films for possible energy applications. The key attributes that we intend to explore are as follows: 1) nanoparticle-modification strategies to provide enhanced catalytic capabilities and increased conductivity, and 2) photo-interferometric fabrication methods to produce highly porous (meso-, micro-, and nano-) and 3D electrode structures. The resulting electrode can be tailored for specific applications and integrated into battery and sensing platforms. Through this work, we will determine which investment area the novel films will most impact, whether the impact will be most evident for fuel cell systems with high catalytic surfaces, nanowires, or novel nanomaterials.

Summary of Accomplishments:
We characterized the conversion of submicrometer resist patterns created using interferometric lithography (IL) to create 3D, highly interconnected porous carbon structures. We showed that the pore sizes in the resulting 3D electrodes were large enough to preserve hemispherical diffusion, resulting in increased mass transport of fuels and analytes; this was demonstrated for methanol oxidation, which should lead to higher energy densities and power outputs for batteries and fuel cells. We also showed the structures as suitable scaffolds for the deposition of conducting polymers and metal nanoparticles. The films on the conducting polymer-coated structures could be controlled to tailor their capacitive properties. The metal nanoparticle modifications were shown to be suitable for catalytic applications and to create hydrogen storage devices.

Significance:
The high mass transport properties of the structures would be useful for the construction of thin battery technologies that require small areas with high energy outputs. Potential applications include micro batteries, fuel cells, capacitors, or hydrogen storage devices.

Refereed Communications:
X. Xiao, M.E. Roberts, D.R. Wheeler, C.M. Washburn, T.L. Edwards, S.M. Brozik, G.A. Montaño, B.C. Bunker, D.B.Burckel, and R. Polsky, "Increased Mass Transport at Lithographically Defined 3D Porous Carbon Electrodes," *ACS Applied Materials and Interfaces*, vol. 2, pp. 3179-3184, October 2010.

D.B. Burckel, C.M. Washburn, D.D. Koleske, and R. Polsky, "Pyrolysis of Two-dimensional and Three-dimensional Interferometrically Patterned Resist Structures," *Journal of Vacuum Science and Technology B*, vol. 28, pp. C6P14-C6P17, October 2010.

X. Xiao, S.M. Brozik, G.A. Montaño, C.M. Washburn, D.R. Wheeler, D.B. Burckel, and R. Polsky, "Non-Limiting Hydrogen Electrosorption Properties of Asymmetric Palladium Nanoparticle-Modified Porous Carbon Electrodes," to be published in *Electroanalysis.*

Room Temperature Detector Array Technology for the Terahertz to Far-Infrared
149404

Year 2 of 2
Principal Investigator: E. A. Shaner

Project Purpose:
The terahertz (THz) to far-infrared portion of the electromagnetic spectrum extends from roughly 100 GHz to 30 THz (where 1 THz corresponds to a wavelength of 300 microns and photon energy of 4.1 meV). From radio-frequency waves through x-rays, this portion of the electromagnetic spectrum is the least developed and, therefore, the least understood scientifically and technologically. Detection of THz radiation at elevated temperatures is complicated due to the low excitation energies involved (ruling out more standard semiconductor-based detection schemes). Our goal in this effort is to develop a path towards room temperature detector solutions that are amenable to integration in a focal plane array.

Our detection platform is based on resonant silicon microphotonics combined with metamaterial absorbers. The platform has been tested in the 8–12 micron wavelength range and had competitive sensitivity and speed compared to room temperature microbolometers while having much higher response times. Under this effort, we are modifying the platform to obtain better absorption in the 8–12 micron spectral range by using vertical cavity enhancement. At the same time, we are moving forward on the concept of integrating metamaterial resonant absorbers for room temperature THz detection.

Summary of Accomplishments:
We successfully demonstrated metamaterial enhanced thermal detection. This approach potentially enables microbolometers to operate in previously unavailable spectral ranges as well as providing spectral selectivity to detection. We also confirmed the sensitivity of the thermal microphotonic microbolometer sensors. A time constant of 2 ms was measured along with a $D^*=2.47 \times 10^8$ cm·√Hz/W. This sensitivity is competitive with commercial microbolometers, while being approximately 5 times faster.

Significance:
Thermal imaging would greatly benefit countermeasure applications and bolster DOE scientific discovery. The need for infrared sensing of biological and chemical materials has also gained in importance in protecting our nation under the Department of Homeland Security strategic plan. Here, thermal imaging may play a role in reaching new levels of sensitivity or improved detection schemes.

Refereed Communications:
H. Tao, E.A. Kadlec, A.C. Strikwerda, K. Fan, W.J. Padilla, R.D. Averitt, E.A. Shaner, and X. Zhang, “Microwave and Terahertz Wave Sensing with Metamaterials,” to be published in *Optics Express*.

Attosat Lorentz Augmented Orbit (LAO) Flight Dynamics
150115

Year 2 of 2
Principal Investigator: J. A. Palmer

Project Purpose:
The term, "attosat", describes a novel category of microchip-sized satellite (with mass not exceeding 0.01 kg) currently under R&D. In addressing the technological challenges, we are motivated by the desire to radically reduce size, weight, and power by maneuvering an attosat without stored liquid or gas-phase propellant. An orbiting attosat moves with tangential velocity v_{rel} relative to the Earth's geomagnetic field which rotates with the planet. If the attosat acquires an electrostatic charge q, the moving geomagnetic field induces the Lorentz force that acts upon the attosat. By this mechanism, the kinetic energy of the Earth's rotation is indirectly converted to useful work. It follows that in specific orbits, an attosat may be propelled via the Lorentz force by modulating the electrostatic charge, the magnitude of which is impacted by parameters to be studied and optimized for the desired propulsion effect, such as mass, materials, geometry, and interactions with the ionosphere's neutral magnetized plasma. To date, detailed and traceable attosat mission scenarios based on effective Lorentz Augmented Orbit (LAO) propulsion technology have yet to be investigated and advanced. In this two-year effort, we are quantifying traceable mission scenarios for attosat deployment, including targets and effects, a launch concept, and requirements for key maneuvers; and execute a model-based engineering physics study to optimize efficient mechanisms for electrostatic charging of an attosat considering plasma interactions.

Summary of Accomplishments:
Efficient mechanisms for negative and positive electrostatic charging of a so-called attosatellite were quantified, considering material, geometry, and emission interactions with the ionosphere's neutral plasma with characteristic Debye length. A novel model-based plasma physics study was undertaken to optimize the positive charge mechanism quantified by the system charge-to-mass ratio. In the context of the practical system design that was established, a positive charge-to-mass ratio on the order of 1.9×10^{-9} C/kg is possible with maximum spacecraft potential equal to the sum of the kinetic energy of electrons from active field emission (+43 V) and less than +5 V from passive elements. The maximum positive potential is less than what is possible with negative electrostatic charging.

Significance:
Propellant-less propulsion of attosats ensures future access to high-payoff space protection, distributed sensing, and emplacement and sampling missions. Results support the conjecture that propellant-less propulsion by LAOs with a charge-to-mass ratio on the order of 1.9×10^{-9} C/kg is possible with positive electrostatic charging by electron field emission. Due to variations in the ionosphere and geomagnetic field, charge-to-mass ratio also varies in the course of an orbit, and as such, future effort should focus on mapping charge-to-mass ratio versus orbital position and altitude considering a magnetized plasma with reasonable use of computational resources. The affordable attosat described here enables access to new, high-payoff missions including distributed sensing, space protection, orbital access, and emplacement and sampling. Moreover, the inherent low ballistic coefficient opens the possibility of a system that may be configured for nondestructive re-entry for practical sample recovery missions. Finally, the attosat system can be mass-produced and configured with existing semiconductor fabrication and test infrastructure.

Refereed Communications:

J.A. Palmer, T.P. Hughes, J.J. Boerner, and G.R. Bennett, "Engineered Plasma Interactions for Geomagnetic Propulsion of Ultra Small Satellites," to be published in *AIAA Journal of Propulsion and Power*.

High-resolution (Sub 50-nm) 3D, In situ Nano-Fabrication of Conductive Elements Within Insulators Using Point Spread Function (PSF) Engineered Lithography or Thermal Heating
154764

Year 1 of 1
Principal Investigator: G. R. Bogart

Project Purpose:
There exists no reasonable, inexpensive approach to deliver electrically conductive nanostructured components in a 3D direct-write fashion capable of sub-50 nm features on any substrate. Such capability would allow for the use of nanoprobe techniques in failure analysis that would be reconfigurable. Also, with the 3D nature of the technique, multiple contacts could be made to the surface of a device. The size of electrical lines could be controlled and processed with results similar to a front-side interconnect scheme. Additionally, current systems that use reactive chemistries to deposit oxides and platinum metal using laser heating may not be reversible.

We are investigating the use of a unique polymer system that is a dielectric in its natural state, but when activated by heating or ultraviolet (UV) light, renders the system conductive. The technique would expand beyond the obvious needs for nanoprobing current dense feature arrays. The need for a direct-write 2D-/3D-capable system with integrated modeling and appropriate photosensitive materials is becoming apparent to researchers and engineers doing integrated circuit fabrication, to make it suitable for next-generation lithography (NGL). Best technologies for NGL, such as extended ultraviolet and scanning electron processes, have been plagued by exaggerated claims of performance and readiness and they are cost prohibitive. They also lack a 3D capability and require planar surfaces. While some direct-write systems are commercially available, features are limited to 600 nm and the approach will likely never meet future needs. The primary failures identified to date that prevent industry and university researchers from delivering 3D direct-write nanostructures include inadequate understanding of how to engineer the photosensitive materials and how to effectively model them. Structure prediction and modeling with direct-write systems is primarily limited to 2D due to the traditional planar approach used in fabrication strategies.

Summary of Accomplishments:
Our initial experiments have demonstrated successful patterning of a conductive xanthate-based polymer film using multiphoton lithography (MPL). These results provide a foundation for developing a more-robust fabrication approach with the potential for arbitrary 3D patterning of conductive polymer materials. Our research includes, 1) optimization of fabrication parameters, 2) increasing the conductivity of MPL sensitive materials, and 3) development of procedures for 3D microstructure fabrication using solution-based precursors (as opposed to spin-coated films) or thicker cast films. Modeling and point spread function calculations will require better characterization of films before that work can begin. For optimization studies, a systematic evaluation of multiphoton excitation (MPE)-induced polymer curing should be performed. Doping the precursor solution with photoinitiator demonstrated the feasibility of MPL photocuring the xanthate precursor polymer into a conductive material. However, a systematic study of concentrations of photoinitiator and laser fluence should be performed. Further, MPE routes to cure the precursor polymer that involve use of common sensitizers such as isopropylthioxanth-9-one (ITX), as opposed to radical generating initiators, should be evaluated as well. Post-processing procedures for increasing the conductivity of the polymers have yet to be evaluated for MPL materials and are expected to increase the conductivity similarly to what has been

shown for the UV-cured system. Optimization studies should lead to formation of higher-quality conductive films. Further, by taking advantage of localized heating generated during MPL fabrication, xanthate elimination followed by thermal curing could potentially occur in a single fabrication step to enable a rapid, high-throughput process. The potential to develop 3D freestanding, electronically active nanomaterials would impact a broad range of applications spanning microfluidics and sensors, as well as energy harvesting, storage, and conversion devices. Our preliminary results indicate a fruitful pathway forward, leading to the development of high value and broadly applied technologies.

Significance:
The proposed work addresses aspects of national security and energy security. The ability to perform 3D interconnects for nanoprobing in a single direct-write mode will allow for unique wiring on a chip-by-chip basis (security). Printing nanoscale subwavelength features on curved surfaces such as "moths' eyes" can enable more efficient imaging (security) and energy collection optics, across all wavelength ranges — including visible — where feature sizes are too small to currently fabricate the ideal period and shape. Other nanostructures such as metamaterials could be fabricated on curved surfaces and in a post-processing manner.

Application-Specific Micro-Ion Trap Development for Mass Spectrometry of Atmospheric Molecules Important to Climate Change

155092

Year 1 of 1
Principal Investigator: M. Mangan

Project Purpose:

The goal of this research is to explore the ability to design a micro-ion trap array based upon traps that differ in their dimensions, but driven by a common radiofrequency(RF). This would enable a new class of miniature mass spectrometers designed for specific applications, including atmospheric molecule detection. Through the selection of trap dimensions, the mass range can be specified. Therefore, by having an array consisting of multiple traps of differing dimensions, the mass ranges can be tailored for a specific application. An example is the atmospheric monitoring of sulfur-containing compounds (SO_2, OCS, CH_3SCH_3) or carbon-containing compounds (CO, CO_2, CH_3, volatile organic compounds, biogenic compounds.) In this example, each trap dimension is chosen to select a small range of mass-to-charge ratios relevant to the problem. In doing so, the trap acts as a mass notch-filter, eliminating unwanted masses and allowing those of interest to accumulate, resulting in a boost in the signal-to-noise ratio for the ions of interest. Additionally, since the dynamical range is reduced, the time required for scanning the mass ranges is reduced, improving time required for data collection. This study will investigate issues of mass resolution, dynamical range, limitations due to manufacturing tolerances and expected signal-to-noise ratios. Quantifying these attributes will demonstrate a core technology that can be applied to a wide array of applications.

Reducing the size and power requirements of mass spectrometers is an active field of research due to the sensitivity and specificity of mass spectrometers, and there is applicability to a wide array of current activities (e.g., explosive detection, atmospheric modeling, health care/biological applications.) Most miniaturization efforts have focused on miniaturizing vacuum components, electronics, etc., but have accepted macroscopic mass separation technologies. Through working with micro-ion traps in conjunction with microfabrication technology, we can reduce the size of this important component while addressing some of the limitations resulting from component miniaturization.

Summary of Accomplishments:

We developed a concept for designing an application-specific ion trap array for mass spectrometry. This concept utilized the facts that the dimensions of an ion trap determine the mass trapping range and the frequency of resonant mass ejection for fixed operational parameters. Using the dimensions of the traps in an array, the trapping mass range is selected for trapping the mass ranges of interest and the resonant mass ejection frequency is selected such that over a short range of secondary RFs, all the relevant ions are ejected. Using this concept, an ion trap array can be designed to efficiently detect a molecular species of interest.

To develop this concept, we numerically modeled the ideal cylindrical ion trap. Using the results of that model, we determined two differing ion trap dimensions that allowed for a proof-of-concept demonstration for the concept of an ion trap array composed of two different-dimension traps, such that the array could be tailored for a specific mass spectrometry application. Using the two different dimension traps, a prototype trapping array structure was designed and constructed. The prototype ion trapping array structure was made of components made of a thin sheet of copper with features formed through photo-chemical etching with a commercial vendor, E-Fab. Two different trapping arrays were constructed, each having two endcap arrays and a ring electrode array. Dimensions were chosen to keep the stack heights of the two different arrays identical. Both arrays were packaged onto a common housing. A common RF source and common secondary RF source with DC offset was used to drive the composite trapping array structure. Tests were conducted on the trapping array structure. We successfully trapped ions. Due to limitations on time, resonant mass ejection was not achieved.

Significance:

The concept of a tailored array of micro-ion traps is an enabling technology development. The impact will extend into other mass spectrometry applications requiring a highly specific point sensor. Areas of direct interest to Sandia include nonproliferation (monitoring effluent released in fuel reprocessing, such as isotopes of xenon), homeland security (explosive and narcotic detection), and nuclear forensics (radioactive material identification.)

Realization of Practical Ultrashort Pulse Laser Technology Through Sandia's All-Fiber Saturable Absorber
155326

Year 1 of 1
Principal Investigator: B. S. Soh

Project Purpose:
The introduction of practical technology for the generation of ultrashort laser pulses (e.g.,100 fs) has long been awaited by numerous important real-world applications. Although ultrashort pulse laser (USP) technology was pioneered in the 1970s and has been the subject of intensive research ever since, and despite the enormous potential payoff of candidate applications, development of technology suitable for use outside the laboratory has proved elusive. The previously developed technology relies on either free-space optics, which does not ensure the practical field deployment, due to long term alignment drift, or fiber-based technology, which uses an unreliable mode-locking device.

In July of 2010, we experimentally demonstrated a new and revolutionary optical component, the all-fiber saturable absorber, which we hypothesize is the key to realizing the promise of USP laser technology. We will attempt to prove, via a combination of experimental demonstration and mathematical modeling, that Sandia's all-fiber saturable absorber enables a self-starting, reliable, environmentally robust, and cost-effective USP laser, and is, in fact, capable of spurring the proliferation of USP laser technology in a wide variety of real-world applications. Once we demonstrate a practical UPS laser oscillator using the proposed device, we can further develop many applications, germane to many fields, including defense, homeland security, medical and fundamental science.

Summary of Accomplishments:
We investigated the feasibility of using the fiber amplitude discriminator (FAD) device for passively mode-locking fiber lasers. During the course of research, we learned that the mode-locked fiber lasers may not tolerate a large amount of optical nonlinearity, which is required to turn on the original FAD saturable absorber. Moreover, when the device length becomes long, it may not provide a robust functionality over time.

We first researched the tolerable amount of optical nonlinearity in a mode-locked fiber laser through studying the semiconductor saturable absorber mirror (SESAM)-based mode-locked fiber laser. Using a SESAM based mode-locked laser as a model, we learned experimentally that the fiber laser cavity may not tolerate more than 1.5 pi radian of nonlinear phase shift. However, with this amount of nonlinearity, the original design of four FAD-device fiber saturable absorber would produce only 0.1% transmittivity. Moreover, the long-term robustness of a long FAD device was tested and found to be unstable for a several meter long FAD device.

We developed an innovative redesign of the FAD device. In the new configuration, a Faraday rotator mirror recycles the input fiber as the output fiber of a zero-order zero-wave plate. It effectively canceled temporal fluctuation of the beat length of the polarization maintaining (PM) fiber and provided a robust functionality. Additionally, a quarter-wave plate is inserted to translate the saturating transmission curve of the FAD device laterally, meaning that we now can change the ground-level transmission freely. One can also change the slope of the transmission curve by changing the coupling angle of PM fiber against the polarization angle of the input linearly polarized light. Through these innovations, a desired transmission curve from the modified FAD device was theoretically and experimentally demonstrated, which is promising for a successful passive mode-locking of the fiber lasers through the FAD device.

Significance:
Although there have been extensive efforts to develop self-starting passively mode-locked fiber lasers, due to their compactness, robustness, and high energy efficiency, thus far, none of the developed methods either successfully replaced Ti:sapphire femtosecond laser systems or were deployed in important application areas. This is the case because of the lack of suitable mode-lockers (i.e., saturable absorbers) that enable self-starting of mode-locked fiber lasers without degradation. All currently available saturable absorbers suitable for fiber lasers are either non-self-starting or degrading over time. On the contrary, our suggested and developed method enables both goals: self-starting and non-degradation. The feasibility is proved through comprehensive theoretical and experimental verifications through this project.

Femtosecond pulses are versatile as a source for generating other optical sources. Examples are supercontinuum generation through wave-mixing/Raman processes in nonlinear material, mid-infrared generation through optical parametric oscillators/amplifiers, THz source generation, and harmonic optical frequency generation towards deep ultraviolet (UV) or x-rays. All of these versatilities come from the fact that the femtosecond pulses have a large peak power that can induce various optical nonlinearities. The overall goal of this ongoing effort to develop self-starting passively mode-locked fiber lasers is to realize an ultrashort pulsed laser source in a rugged platform for mobile environments. Although the Ti:sapphire lasers have been extensively used for development of applications based on femtosecond pulsed lasers, the bulky and environmentally sensitive nature of such laser systems have prevented widespread deployment of femtosecond pulsed laser systems.

Once demonstrated, the passively mode-locked fiber lasers based on the FAD device will be widely and extensively used in the already developed applications of femtosecond lasers. These include,

- Material processing in high-precision microelectromechanical systems (MEMS)
- Numerous medical applications including surgery, breath analysis, multiphoton imaging, etc.
- Remote sensing and non-invasive human body detection through THz wave systems
- Infrared countermeasures
- High-speed optical communication

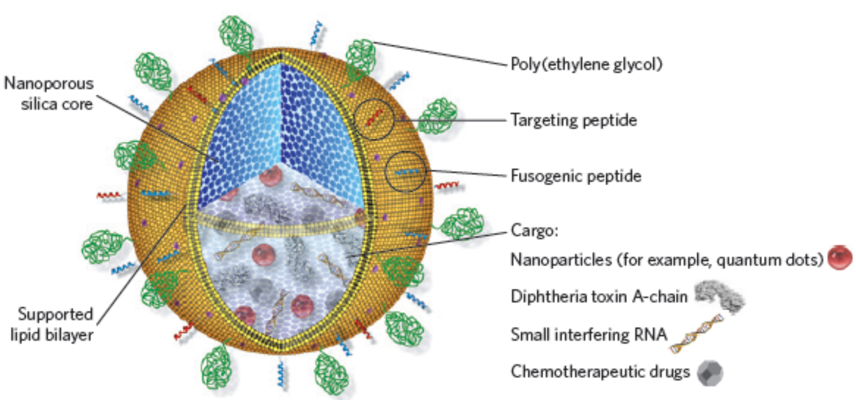
If successful, this work will generate productive activity in both the applied and theoretical realm of ultrashort pulse (USP) laser technology. There should also be numerous opportunities for follow-on development.

STRATEGIC PARTNERSHIPS INVESTMENT AREA

The common defining feature of projects in this investment area (IA) is a strong cooperative research endeavor with one or more academic or corporate partners. Because of Sandia's leadership in the multipartner National Institute for Nano Engineering (NINE), many SP projects are found in the nanotechnology arena. In addition, other projects within this IA, include the Sandia Fellows, and the President Harry S. Truman fellows, awarded annually to two or three recipients. In addition to being a great honor, the Truman is unique in that it supports a three-year initiative to pursue leading-edge research defined by the candidates own proposal, which must be consonant with one or more of Sandia national security missions but which otherwise provides significant intellectual leeway.

Nature Versus Nurture in Cellular Behavior and Disease
Project 141704

Among its other discoveries that enable biomineralization and conversion of biological structures to function-retaining silicon equivalents, this project also presents an evolved route to the possible outcome of single-dose killing of cancer cells. Dubbed "protocells," this ingenious nanoparticulate engineering of organic and inorganic materials goes one better on liposomes, an already FDA-approved method of drug delivery. While a liposome is simply a bag of aqueous solution encapsulated by a ligand-decorated lipid-bilayer membrane (the same type of membrane that encloses all higher (Eukaryotic) cells and many of their internal organelles, a protocell is much more. The outer lipid bilayer bag encloses a nanoporous silica nanoparticle that acts as a high-surface-area container-binder for a diversity of cytotoxic compounds—drugs, nucleic acids (such as small inhibitory RNAs [siRNA]), proteins, and peptides of varying water solubility, some of which are difficult to simply dissolve in the aqueous medium of liposomes. Additionally the membrane of the protocell is "decorated" with both specific and nonspecific binding agents (peptide ligands) that stick it to receptors on a given cancer cell's surface (in this instance, hepatocarcinoma) and promote its internalization into the cancer cell (via a process known as receptor-mediated endocytosis), wherein it releases its huge cargo of cytotoxins, a cargo that can be composed of such a disparate array of compounds—in terms of mechanism of action—that the probability of a kill is maximized, while the probability of the cancer cell's developing drug resistance is minimized. Wrapping the lipid bilayer around the silica nanoparticle imparts highly desirable physical characteristics to the fluidity and stability of the lipid bilayer—favoring its highly specific binding to the cancer cell's surface, a prerequisite for internalization (endocytosis), and lowering its side-effect profile in binding to and killing normal cell types—in this instance, normal liver cells (hepatocytes). In addition, the surface of the protocell is engineered such that it is quite soluble in blood and is tailored toward low immunogenicity, that is, it does not strongly stimulate the immune system to act against and remove it,



Schematic drawing of protocell created in this project, showing lipid bilayer surrounding a nanoporous silica core carrying a cargo of chemical and biological agents toxic to cancer cells.

both key characteristics of an effective agent in vivo. Although in vivo testing yet lies in the future, the in vitro results are stunning, showing that a single nanoparticulate protocell can deliver such a potent dose of cytotoxic agents so as to be effective at killing a hepatocarcinoma cell with a single dose, while sparing greater than 90% of normal liver hepatocytes.

Cosmic-ray Hydrometrology for Land Surface Studies
Project 120208

At a time when climate change and other factors such as human population growth threaten to challenge the availability of potable water and other water resources, a comprehensive understanding of the availability, breadth (or limitations) and nature of water resources constitutes critical knowledge. Efforts to explore this knowledge using the cosmogenic neutrons that are routinely produced in earth's atmosphere employ a naturally occurring sensor to detect certain of those resources, among which snow cover and soil moisture are of great importance. When a cosmic ray from space strikes an atom in earth's atmosphere, a cascade of elementary particles results, and this so-called "nucleonic cascade" can ultimately be used in detection of surface water.

This project performed first-of-their kind measurements, modeling and theoretical work in order to advance the technique of measuring soil moisture and snow with cosmic-ray neutrons. The technique is slated to be utilized in a national soil moisture monitoring network by 2015.

A probe installed at the Valles Caldera, a volcanic bowl in northern New Mexico, is the first cold-weather installation in the world. It was used to demonstrate applications to measurements of snow pack, and to determine the limit of snow depth measurements that could be performed with the probe.

Neutron detector installed for field studies in northern New Mexico

Strategic Partnerships Investment Area

Cosmic-Ray Hydrometrology for Land Surface Studies
120208

Year 4 of 4*
Principal Investigator: D. Desilets

Project Purpose:
Energetic cosmic rays continually bombard Earth, with implications important to humanity. For example, cosmic rays interact with microelectronic components, generating soft errors in advanced computing systems and posing challenges to the design of reliable aerospace components. Cosmic rays also interact with materials in the upper meter of Earth's crust, producing rare radionuclides that are retained in the lattices of rock minerals. The buildup of these radionuclides (e.g., ^{10}Be and ^{36}Cl) can be used to determine numerical ages of previously not datable geologic hazards such as prehistoric earthquakes, volcanic eruptions and landslides. Cosmic rays also produce rare radionuclides in the atmosphere, providing a valuable tracer for atmospheric transport and mixing processes. Investigators at Los Alamos National Laboratory have shown that highly penetrating cosmic rays can be used as an imaging tool to locate fissile materials hidden in shipping containers. More recently, the utilization of cosmic rays has been extended to the field of hydrology, where it has been discovered that measurements of slow cosmic-ray neutrons can potentially be used to remotely and passively monitor soil water content and snow water equivalence at a footprint not attainable by other instruments. This project is centered on the novel application of cosmic rays to remote sensing of soil water content and snow water equivalence — two of the most important variables in the hydrologic cycle. This new technology can be put to a variety of uses, including monitoring slope stability, forecasting spring snow melt and flash floods, and monitoring soil moisture in croplands. In addition to exploring applications in hydrology, this project is investigating fundamental aspects of cosmic-ray physics and neutron transport and, therefore, potentially provides ancillary benefits to all areas of applied cosmic ray research. The project PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments:
In this project, we performed first-of-their kind measurements, modeling and theoretical work in order to advance the technique of measuring soil moisture and snow with cosmic-ray neutrons. The technique is expected to be utilized in a national soil moisture-monitoring network by 2015.

A probe installed at the Valles Caldera is the first cold-weather installation in the world. It was used to demonstrate applications to measurements of snow pack, and to determine the limit of snow-depth measurements that could be performed with the probe. A new application to the determination of snow-canopy water was demonstrated as part of this work.

Data from paired catchments in Santa Fe, New Mexico, showed that even catchments with markedly different canopy cover can have similar hydrologic responses. Data from Santa Fe also demonstrate the advantage of spatial averaging in soil moisture determinations and, therefore, support the use of this technique wherever soils are heterogeneous.

*This 36-month project spanned four fiscal years

Theoretical work resulted in the derivation of a shape-defining calibration curve for soil moisture determinations. This theoretical curve was then parameterized using neutron transport simulations. A combination of modeling and theory was used to determine the radius of influence and penetration depth for this technique, and to derive an optimal field-sampling plan.

Significance:

The project is developing tools and techniques that will be crucial to accurately understanding and predicting the availability of water for energy production and myriad other competing uses of this precious resource. The research also has strong potential impact in other mission areas of importance to DOE, including climate change, homeland security (detection of trace radioactivity), and nuclear transport theory and application.

Refereed Communications:

D. Desilets, M. Zreda, and T.P.A. Ferre, “Nature's Neutron Probe: Land Surface Hydrology at an Elusive Scale with Cosmic Rays,” *Water Resources Research*, vol. 46, p. W11505, November 2010.

Computational Models of Intergroup Competition and Warfare
130810

Year 3 of 3
Principal Investigator: R. G. Abbott

Project Purpose:
Warfare is an extreme form of intergroup competition in which individuals make extreme sacrifices for the benefit of their nation or other groups to which they belong. It is not fully understood what factors lead to warfare, or to more moderate examples of intergroup competition like territorial fighting in social primates. Building on agent-based models of ant foraging, graduate research fellow Kenneth Letendre, at the University of New Mexico, developed models of inter-colony conflict in ants, and studied conflict and warfare among human groups. He developed a genetic algorithm to model the coevolution of conflict behaviors in ant colonies and group-living humans. These powerful computational techniques provide novel insights and allow us to test hypotheses about what drives intergroup competition and warfare. Research in this project focused on the development of computational models of intergroup competition. In particular, we studied the conditions under which natural selection accounts for the following traits: optimal group size, balancing the need to disperse for access to new food sources against the benefits of living in large groups, such as information sharing and strength of numbers; individual sacrifice for the benefit of the group (altruism); and how changes in the intensity of intergroup competition over time applies pressure for the attunement of effort devoted to individual vs. group goals, both over the course of generations, and within the lifetime of an individual. There is a tradition of examining these properties using mathematical and computational models. However, these models have failed to take advantage of genetic algorithms to simulate the evolution of intergroup aggression by natural selection. The emergent properties of groups of organisms lend themselves to study using computational models because group properties are the result of the repeated interactions of discrete, individual members of those groups.

Summary of Accomplishments:
The first component of this project was a study of the global variation in the frequency of civil conflict among countries of the world, and its positive association with variation in the intensity of infectious disease. We demonstrated that the burden of human infectious disease importantly predicts the frequency of civil conflict (Letendre, et al., 2010; Letendre, et. al, in press) and tested a causal model for this association based on the parasite-stress theory of sociality (Letendre, et al., in press).

The parasite-stress model of sociality applied to civil war was supported (Letendre, et al., 2010). The statistical analyses and their empirical results indicated that pathogen severity positively predicted the frequency of civil-war outbreaks across the globe, and this was found in separate analyses for small-scale conflicts with relatively low mortality, as well in large-scale civil wars with high mortality.

Finally, we examined the application of the parasite-stress model to a measure of peace vs. conflict across countries, the Global Peace Index. We found that the incidence of intrastate-armed conflict, non-state wars, and revolutions and coups was predicted by parasite stress. These results are robust across a variety of categories of conflict, even when controlling for a battery of demographic, economic, and political indicators.

The second component of this project was an investigation into the organization of social foraging by colonies of harvester ants in the genus, *Pogonomyrmex*. According to optimal foraging theory, animals evolve behaviors that maximize energy gain and minimize foraging costs given the distribution of food in their environment. We investigated how the entropy of food distribution affects foraging rates in field studies and models of three sympatric species of harvester ants of the genus, *Pogonomyrmex*. The integration of models and field studies led to insights that neither could achieve in isolation.

Significance:
Our work discovered factors that contribute to the timing, intensity, and distribution of cooperation and warfare. The models study the emergence of group properties and behavior as the result of the interaction of individuals, clarifying the contribution of individual psychology and motivation to the occurrence of warfare. This research has also contributed enhancements to Ant Colony Optimization, an algorithm with application to a broad range of design and analysis tasks.

Refereed Communications:
T.P. Flanagan, K. Letendre, W.R. Burnside, G.M. Fricke, and M. Moses, "How Ants Turn Information into Food," *Proceedings of IEEE Symposium on Artificial Life,* pp. 178-185, 2011.

K. Letendre, C.L. Fincher, and R. Thornhill, "Does Infectious Disease Cause Global Variation in the Frequency of Intrastate Armed Conflict and Civil War?" *Biological Reviews*, vol. 85, pp. 669-683, August 2010.

K. Letendre, C.L. Fincher, and R.Thornhill, "Infectious Disease, Collectivism, and Warfare," *Oxford Handbook on Evolutionary Perspectives on Violence, Homicide, and Warfare*, T. Shackelford, and V. Weekes-Shackelford, eds., Oxford University Press, 2011.

Development and Characterization of 3D, Nano-Confined Multicellular Constructs for Advanced Biohybrid Devices
130813

Year 3 of 3
Principal Investigator: B. J. Kaehr

Project Purpose:
Inspiration for the design of new materials and devices is increasingly found in biological systems where sensitive detection, energy conversion, and molecular/nanomachinery have been continually improved upon by evolution. However, to impart the useful properties of biological systems into devices requires new ideas and technologies. Although there has been much focus on material functionalization using biomolecules, incorporation of self-sustaining and self-replicating components (e.g., biological cells and bio-catalysts) into solid-state platforms has received scant attention. Moreover, in order to bridge the organic structures and functionalities of cells to the inorganic, solid-state materials of modern devices, functional biotic/abiotic interfaces are required. This project has addressed these problems using a breakthrough approach for the rapid-prototyping of 3D bio-interfaces and catalytic architectures. The project PI is a President Harry S. Truman Fellowship recipient.

In this work, recent breakthroughs in 3D microfabrication that enable the topographical and chemical microenvironments of developing cell populations to be precisely defined (Kaehr & Shear JACS 2007, PNAS 2008, Lab on a Chip 2009) and analyzed (Khripin, Brinker & Kaehr, Soft Matter 2010) were employed to confine and direct the behaviors of developing cell populations and develop new biohybrid materials based on "diatometic" chemistry (Khripin, Pristinski, Dunphy, Brinker and Kaehr, *ACS Nano*, 2010). Patterning of biological architectures and cellular constructs that can direct assembly of inorganic materials combined with the emerging tools of cellular (re)programming (i.e., synthetic biology) provide a foundation to design communication networks between engineered cell populations — enabling the development of cell-based circuitry. These efforts should expand the applications of biohybrid materials into new territories. For instance, sensing regimes based on precisely defined cell behaviors (e.g., cell motility) and networked cells communicating via innate and engineered pathways will enhance the range and sensitivity of biosensing devices to analytes in complex environments.

Summary of Accomplishments:
We achieved the following major milestones:

1. We developed a microfabrication approach that allows biocompatible confinement of a broad range of cell types (and their subsequent progeny) within (bio)relevant materials.
2. We developed a quantitative methodology to study the mechanical properties of microfabricated protein hydrogels under dynamic chemical and physical conditions and applied this method to measure the pressure of developing cells confined in engineered microenvironments.
3. We demonstrated a protein-directed approach to template nanoporous silica frameworks into arbitrary 3D architectures by employing crosslinked protein hydrogels to controllably direct silica condensation. We further showed conversion of these porous structures into other device materials such as silicon.
4. We pioneered a new strategy that employs cell growth to direct formation of functional inorganic/cell interfaces. This discovery demonstrates a new route for Janus (asymmetric) metallic particle synthesis using biotemplates for the synthesis of microscale catalytic motors and pumps.
5. We developed a generalized methodology by which to construct biomorphic nanocomposites from any cell type. We showed that this simple procedure can be used to make conductive (carbonized) replicas of the interior cellular architecture.

Significance:
Biological chemistries, cells, and integrated systems (e.g., organisms, ecologies, etc.) offer important lessons for the design of synthetic strategies and materials. The desire to both understand and ultimately improve upon biological processes has been a driving force for considerable scientific efforts worldwide. However, to impart the useful properties of biological systems into modern devices and materials requires new ideas and technologies. The work generated by this research addresses significant aspects of these issues through the development of 1) a rapid-prototyping methodology to build 3D bio-interfaces and catalytic architectures, 2) a quantitative method to measure cell/material mechanical interactions in situ and at the microscale, and 3) a breakthrough approach to generate functional biocomposites from bacteria and cultured cells.

Overall, this work bridges a number of areas spanning biology and materials science and provides a foundation to both understand and integrate biological systems into materials and devices. The new technologies described here to prototype 3D inorganic and cell-based device materials can be used as a platform to explore a broad range of applications including photonics, plasmonics, metamaterials, biocatalysts, sensors, and decontamination systems.

Refereed Communications:
J.C. Harper, C.Y. Khirpin, E.C. Carnes, C.E. Ashley, D.M. L**ó**pez, T. Savage, H.D. Jones, R.W. Davis, L.M. Brinker, B.J. Kaehr, S.M. Brozik, and C.J. Brinker, "Cell-Directed Integration into 3D Lipid-Silica Nanostructured Matrices," *ACS Nano*, vol. 4, pp. 5539–5550, October 2010.

P.E. Hopkins, B.J. Kaehr, L.M. Phinney, T.P. Koehler, A.M. Grillet, D.R. Dunphy, F.L. García, and C.J. Brinker, "Measuring the Thermal Conductivity of Porous, Transparent SiO_2 Films with Time Domain Thermoreflectance," *Journal of Heat Transfer*, vol. 133, p. 061601, June 2011.

D.R. Dunphy, F.L. García, B.J. Kaehr, C.Y. Khripin, A.D. Collord, H.K. Baca, M.P. Tate, H.W. Hillhouse, J.W. Strzalka, Z. Jiang, J. Wang, and C.J. Brinker, "Tricontinuous Cubic Nanostructure and Pore Size Patterning in Mesostructured Silica Films Templated with Glycerol Monooleate," *Chemistry of Materials*, vol. 23, pp. 2107–2112, March 2011.

C.Y. Khripin, D. Pristinski, D.R. Dunphy, C.J. Brinker, and B.J. Kaehr, "Protein-Directed Assembly of Arbitrary Three-Dimensional Nanoporous Silica Architectures," *ACS Nano*, vol. 5, pp. 1401-1409, January 2011.

L.D. Zarzar, P. Kim, M. Kolle, C.J. Brinker, J. Aizenberg, and B.J. Kaehr, "Direct Writing and Actuation of Three-Dimensional Patterned Hydrogel Pads on Micropillar Supports,"*Angewandte Chemie International Edition*, vol. 50, pp. 9356–9360, September 2011.

Development of a Structural Health Monitoring System for the Assessment of Critical Transportation Infrastructure
130814

Year 3 of 3
Principal Investigator: D. P. Roach

Project Purpose:
Recent structural failures such as the I-35W Mississippi River Bridge in Minnesota have underscored the urgent need for improved methods and procedures for evaluating our aging transportation infrastructure. This research seeks to develop a structural health monitoring (SHM) approach to provide more quantitative information related to the structural integrity of metallic structures to make appropriate management decisions and ensure public safety. The system will employ advanced structural analysis and nondestructive testing (NDT) methods for sensing/measurement and decision-making purposes. Metal railroad bridges in New Mexico will be the focus since many of these structures are over 100 years old and classified as fracture-critical. Fracture-critical indicates that failure of a single component may result in complete collapse of the structure such as the one experienced by the I-35W Bridge. Failure may originate from sources such as loss of section due to corrosion and cracking due to fatigue. Fatigue cracks may not be seen in a typical visual inspection; however, inspectors could be informed of potential fatigue-prone details that are near the end of their theoretical fatigue lives if an appropriate SHM method is applied. Another issue is that it is difficult to determine the load-induced fatigue damage that a structure has experienced and the rate at which damage is accumulating due to uncertain load distribution to supporting members without taking field measurements. A SHM system has several advantages for overcoming these limitations, primarily that critical areas of the structure are monitored quantitatively under actual loading. This research focuses on the evaluation of load-induced fatigue of metallic structures and the development of a SHM approach for assessing the remaining fatigue life of critical transportation infrastructure. This project will combine the expertise in transportation infrastructure at New Mexico State University with the expertise at Sandia in the emerging field of SHM.

Summary of Accomplishments:
A thorough literature review that included fatigue in steel structures, SHM, and bridge management has been completed and documented. The literature showed that fatigue is one of the most common failure mechanisms in metallic structures, and that various methods have been developed to attempt to identify failures in large structures primarily using long-term monitoring with dynamic sensors. Little evidence was found in the literature that a system is available that reliably and accurately locates and quantifies structural damage in the field. This research uses short-term measurements since many sensor types were found to be unreliable for long-term measurements in the literature. Strain measurements are used to determine the service behavior of the structure and to validate a finite-element model (FEM) which can be used to estimate the remaining fatigue life. One structure was load-tested under service loads and the load test data was compared to the simulated responses. It was found that the simulated strains from a basic FEM tend to overestimate the actual strains of the bridge, particularly for the stringers. A more detailed FEM was developed that modeled the ballast on the deck as elastic springs, thus distributing the live load longitudinally. The refined FEM was found to be more accurate for the stringers; however, the simulated floorbeam and girder responses remained essentially unchanged. Of the four FEMs developed, the one simulating the ballast and assuming no fixity at the member ends was found to be most representative for this structure. This model was then used to perform a fatigue evaluation according to the American Railway Engineering and Maintenance-of-Way Association (AREMA) Specification (2007), which resulted in a remaining fatigue life estimate of over 100 years. A framework for a SHM

method based on remaining fatigue life calculations was also developed. All of the work performed was documented in a Sandia Report.

Significance:
SHM shows great promise for various DOE-related areas such as critical infrastructure assurance and homeland security. Although advanced methods and techniques are available to SHM professionals, deployment of SHM systems for in-depth evaluation has been slow due to the lack of specific procedures for properly designing, installing, and operating the SHM system for making decisions. This project will enable more widespread use of SHM to improve the assessment of our critical infrastructure.

Evaluation of Baseline Numerical Schemes for Compressible Turbulence Simulations
130817

Year 3 of 3
Principal Investigator: J. Smith

Project Purpose:
Numerical and modeling errors in turbulence simulations are difficult to isolate and quantify. An approach that has previously shown promise in this area is the Method of Nearby Problems (MNP), developed by Presidential Early Career Award for Scientists and Engineers winner, Dr. Christopher Roy of Virginia Technical University. MNP is a novel approach that can be used to assess numerical errors in complex calculations. In MNP, exact solutions are generated by spline fitting highly resolved numerical solutions. These solutions are "nearby" the numerical solutions from which they were derived, and thus are representative of the relevant physical and mathematical properties, yet they are exact and can thus be represented to machine precision. These exact solutions are solutions not to the original equation set, but rather, to a "nearby" equation set, with the same differential operator and a source term generated by applying the original differential operator to the exact solution. The source terms generated are small and distributed, preserving the "nearby" nature of the new equation set. Multidimensional MNP can be applied to problems in code and solution verification in many different areas of computational science and engineering. In addition, MNP can be used to provide discretization error estimates by solving an additional problem on the same grid. This approach is similar to the differential (or continuous) form of defect correction. MNP can thus provide discretization error estimates on a single grid, as compared to approaches such as Richardson extrapolation which require multiple, systematically refined grids to produce error estimates. The MNP procedure is equally applicable to finite difference, finite volume, and finite element methods.

Summary of Accomplishments:
MNP, a form of defect correction, has been examined as a method for generating exact solutions to partial differential equations and as a discretization error estimator. For generating exact solutions, four-dimensional spline fitting procedures were developed and implemented into a MATLAB code for generating spline fits on structured domains with arbitrary levels of continuity between spline zones. For discretization error estimation, MNP/defect correction only requires a single additional numerical solution on the same grid (as compared to Richardson extrapolation which requires additional numerical solutions on systematically refined grids). When MNP was used for error estimation, we found that continuity between spline zones was not required. A number of cases were examined including 1D and 2D Burgers' equation, the 2D compressible Euler equations, and the 2D incompressible Navier-Stokes equations. The discretization error estimation results compared favorably to Richardson extrapolation and had the advantage of only requiring generation of a single grid.

Significance:
This work provides a platform for evaluating numerical schemes for compressible turbulent flows, which are important in a number of transonic and supersonic weapons systems. The work also advances the state-of-the-art in discretization error estimation, which indirectly impacts the predictive capability of modeling and simulation for the Stockpile Stewardship mission. This capability addresses a key need in the modeling and simulation community.

Refereed Communications:

C.J. Roy, T.S. Phillips, A. Choudhary, and J. Derlaga, "A Residual-Based Framework for Error Estimation and Adaptivity for Finite Volume and Finite Difference Methods," to be published in the *Journal of Computational Physics*.

Interfacial Electron and Phonon Scattering Processes in High-Powered Nanoscale Applications
130818

Year 3 of 3
Principal Investigator: P. E. Hopkins

Project Purpose:
A significant limiting factor in next-generation nanoelectronic systems is the large heat fluxes generated from operation. Inadequate power dissipation capabilities in these systems result in self-heating and increased operating temperatures that degrade device gain and efficiency and shorten device life. The materials used in the design and construction of the nanoelectronic devices and the dissipation of the heat from these devices contributes to overheating. As these nanoelectronic systems continue to decrease in characteristic sizes, the thermal management issues arise at the interfaces or junctions of different materials where thermal energy carrier scattering is prominent. Nowhere is this problem more pronounced than in high-powered systems, such as modern weapon, sensor, and signal processing systems, and energy conversion systems, such as thermoelectric coolers and power generators. The key to thermal engineering of next-generation nanosystems is to understand the intrinsic properties of materials that affect interfacial thermal transport.

The objective of this project has been to study heat transfer processes around structurally imperfect regions at interfaces involving both traditional and novel nanostructures used in high-powered nanoelectronic and energy conversion applications. Deposition, fabrication, and post-possessing procedures of nanocomposites and devices can give rise to interatomic mixing around interfaces of materials, leading to stresses and imperfections that could affect heat transfer. An understanding of the physics of energy carrier scattering processes and their response to interfacial disorder will elucidate the potentials of applying these novel materials to next-generation high powered nanodevices and energy conversion applications. The project PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments:
This project explored mechanisms of thermal transport at interfaces of nanomaterials, specifically linking the thermal conductivity and thermal boundary conductance to the structures and geometries of interfaces and boundaries. This work linked deposition, fabrication, and post-possessing procedures of nanocomposites and devices to heat transfer. The physics of energy carrier scattering processes and their response to interfacial disorder was developed which elucidated the potentials of applying these novel materials to next-generation high-powered nanodevices and energy conversion applications. An additional accomplishment of this project was the ability to control, or “tune” the thermal transport in nanosystems with the interfacial structure.

This project has resulted in 38 refereed journal publications, with an additional two publications currently under review, one in press, and one invited book chapter. Many of these works were centered around measurements of thermal transport in nanosystems with time domain thermoreflectance (TDTR), an ultrashort pulsed laser based pump-probe technique that was developed as part of this project.

Significance:
One key to continued success with national security and defense issues lies in improving the fundamental scientific understanding of the complex dynamic behavior in modern weapon and sensor systems and energy conversion systems used in military applications. With the increased power requirements and heat production in these systems, the behavior of the thermal processes across material interfaces is becoming more critical, especially with the decrease in size of the components of these

systems to the nanoscale. This study has examined the effects of structural disorder around interfaces on thermal carrier scattering events that contribute to thermal boundary conductance, thereby elucidating fundamental physics issues that will be crucial to understand as these systems become further miniaturized.

Refereed Communications:

P.E. Hopkins, "Influence of Inter- and Intra-band Transitions to Electron Temperature Decay in Noble Metals after Short-Pulsed Laser Heating," *Journal of Heat Transfer*, vol. 132, p. 122402, December 2010.

J.C. Duda, T.E. Beechem, J.L. Smoyer, P.M. Norris, and P.E. Hopkins, "The Role of Dispersion on Phononic Thermal Boundary Conductance," *Journal of Applied Physics*, vol. 108, p. 073515, October 2010.

P.E. Hopkins, M.L. Bauer, J.C. Duda, J.L. Smoyer, T.S. English, P.M. Norris, T.E. Beechem, and D.A. Stewart, "Ultrafast Thermoelectric Properties of Gold under Conditions of Strong Electron-Phonon Nonequilibrium," *Journal of Applied Physics*, vol. 108, p. 104907, 2010.

P.E. Hopkins, J.R. Serrano, and L.M. Phinney, "Comparison of Thermal Conductivity and Thermal Boundary Conductance Measurements Using Continuous-Wave and Ultrashort-Pulsed Thermoreflectance Techniques," *International Journal of Thermophysics*, vol. 31, p. 2380, 2010.

P.E. Hopkins, J.R. Serrano, L.M. Phinney, H. Li, and A. Misra, "Boundary Scattering Effects during Electron Thermalization in Nanoporous Gold," *Journal of Applied Physics*, vol. 109, p. 013524, January 2011.

P.E. Hopkins, C.M. Reinke, M.F. Su, R.H. Olsson, E.A. Shaner, Z.C. Leseman, J.R. Serrano, L.M. Phinney, and I. El-Kady, "Reduction in the Thermal Conductivity of Single Crystalline Silicon by Phononic Crystal Patterning," *Nano Letters*, vol. 11, pp. 107-112, November 2010.

P.E. Hopkins, L.M. Phinney, and J.R. Serrano, "Re-examining Electron-Fermi Relaxation in Au with a Nonlinear Thermoreflectance Model," *Journal of Heat Transfer*, vol. 133, p. 044505, April 2011.

P.E. Hopkins, J.C. Duda, and P.M. Norris, "Anharmonic Phonon Interactions at Interfaces and Contributions to Thermal Boundary Conductance," *Journal of Heat Transfer*, vol. 133, p. 062401, June 2011.

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J.C. Duda, C.B. Saltonstall, P.M. Norris, and P.E. Hopkins, "Assessment and Prediction of Thermal Transport at Solid-Self-Assembled Monolayer Junctions," *Journal of Chemical Physics*, vol. 134, p. 094704, March 2011.

J.C. Duda, P.M. Norris, and P.E. Hopkins, "On the Linear Temperature Dependence of Phonon Thermal Boundary Conductance in the Classical Limit," *Journal of Heat Transfer*, vol. 133, p. 074501, July 2011.

S.P.R. Clark, P. Ahirwar, F.T. Jaeckel, C.P. Hains, A.R. Albrecht, T.J. Rotter, L.R. Dawson, G. Balakrishnan, L.M. Phinney, P.E. Hopkins, J. Hader, and J.V. Moloney, "Growth and Thermal Conductivity Analysis of Polycrystalline GaAs on Chemical Vapor Deposition Diamond for use in Thermal Management of High-Power Semiconductor Lasers," *Journal of Vacuum Science and Technology B*, vol. 29, p. 03C130, April 2011.

P.E. Hopkins, L.M. Phinney, P.T. Rakich, R.H. Olsson, and I. El-Kady, "Phonon Considerations in the Reduction of Thermal Conductivity in Phononic Crystals," *Applied Physics A*, vol. 103, pp. 575-579, 2011.

P.E. Hopkins, J.C. Duda, S.P. Clark, C.P. Hains, T.J. Rotter, L.M. Phinney, and G. Balakrishnan, "Effect of Dislocation Density on Thermal Boundary Conductance across GaSb/GaAs Interfaces," *Applied Physics Letters*, vol. 98, p. 161913, 2011.

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P.E. Hopkins, J.C. Duda, C.W. Petz, and J.A. Floro, "Controlling Thermal Conductance through Quantum Dot Roughening at Interfaces," *Physical Review B*, vol. 84, p. 035438, July 2011.

P.E. Hopkins, T.E. Beechem, J.C. Duda, K. Hattar, J.F. Ihlefeld, M.A. Rodríguez, and E.S. Piekos, "Influence of Anisotropy on Thermal Boundary Conductance at Solid Interfaces," *Physical Review B*, vol. 84, p. 125408, September 2011.

P.E. Hopkins, M. Mittal, L.M. Phinney, A.M. Grillet, and E.M. Furst, "Ultra-Low Thermal Conductivity of Ellipsoidal TiO_2 Nanoparticle Films," to be published in *Applied Physics Letters*.

P.E. Hopkins and J.C. Duda, "Introduction to Nanoscale Thermal Conduction," *Heat Transfer – Mathematical Modelling, Numerical Methods and Information Technology,* A. Belmiloudi, ed., In Tech, 2011.

Nanocomposite Materials for Efficient Solar Hydrogen Production
130820

Year 3 of 3
Principal Investigator: J. E. Miller

Project Purpose:
Materials that utilize concentrated solar energy to produce hydrogen will potentially enable a long-term viable alternative to fossil fuels. The goal of this research is to enhance the efficiency of fuel production using solar energy and thermochemical materials. Our approach focuses on manufacturing robust, high-geometric-surface-area substrates into honeycombs with space for deep light penetration in order to enhance the efficiency of thermochemical processes. Advanced ceramic manufacturing methods, such as polymer co-extrusion, are used to provide an improvement over the current generation of materials as the active exposed phase will have a higher surface area to volume ratio within the oxygen-conducting bulk phase that should allow for greater materials utilization within each thermochemical cycle. We are working with a known material formulation based on Fe_3O_4 and $CoFe_2O_4$ as the active phase material and processed into composite mixtures using the substrate materials, 3- and 8-mol% yttria stabilized zirconia. The effect of yttria content in zirconia will be used to partially control the number of oxygen vacancies present in the material in order to investigate the effect of oxygen vacancies used for oxygen transport during the thermochemical reaction process. Oxygen vacancy concentrations will be calculated and compared to thermochemical efficiencies. The composite mixtures will be tested at the National Solar Thermal Testing Facility (NSTTF). Honeycomb structure processing and analysis of test performance will take place in the Materials Science and Engineering Department at The University of Arizona.

Summary of Accomplishments:
- Developed powder processing and polymer co-extrusion methods for Fe_2O_3-ZrO_2 (and nickel ferrite-ZrO_2) with increasing yttria content from 3 to 8 mol% composites.
- Extruded and laminated structures into 1- and 2-cm honeycomb structures with 2-, 4- and 6-mm cell size with wall thickness ranging from 0.2-0.5 mm.
- Designed binder burnout and sintering heat treatments.
- Designed and tested 1-cm test parts in lab scale reactor configuration.
- Analyzed CO production efficiencies of honeycomb test substrates as a function of surface area.
- Designed solar test cycles in order to evaluate honeycomb structure, geometry, and composite thermochemical efficiencies at NSTTF.

Significance:
The design and implementation of new thermochemical materials that have ideal compositions and structures will enable cutting-edge technology for producing alternatives to fossil fuels. This work on sustainable energy sources directly supports the goals of all four DOE strategic areas including Defense, Energy, Science, and Environment, and as such, it will help to strengthen our nation's long-term energy independence and national security.

Nanotexturing of Surfaces to Reduce Melting Point
130821

Year 3 of 3ìí
Principal Investigator: E. J. García

Project Purpose:
The reduced melting point of nanotextured silicon surfaces is far below theoretical prediction and has practical application for bonding in microsystems packaging. This three-year project in collaboration with University of Texas at El Paso (UTEP), focuses on: (Year 1) advancing the science and technology of reduced melting point (RMP) in nanotextured silicon-on-insulator (SOI) wafers; (Year 2) using RMP for bonding applications; and (Year 3) implementing the RMP bonding technique for microsystems. Year 1 research focused on comparing theoretical predictions to results from melting experiments in which the geometry and size of the surface SOI wafers was varied. Preliminary experiments have shown that the melting point of silicon nanocrystals measuring 100 nm in diameter and 40 nm in thickness but with very fine features (< 5nm) is reduced from its bulk value of 1412 °C to 1055 °C. This reduction deviates strongly from simple theoretical modeling that predicts that for a melting temperature of 1055 °C, the particle diameter would have to be ~0.8 nm. In this project, theoretical models were adapted and used to predict the size-dependent melting of nanostructured silicon crystals using the appropriate characteristic dimension such as the size of fine features. An experiment was designed to nanopattern the surface SOI wafers and to heat the samples to determine their size-dependent melting point. The silicon nanocrystals were characterized for morphology, size, and crystallography, before and after heat treatment. Experimental results were analyzed relative to theoretical predictions. Year 2 research studied the effect of doping the surface silicon to further reduce the melting point. Localized heating via electrical current through doped regions was investigated. Bond strength and character are being studied as a function of temperature and pressure. Year 3 implemented the RMP bonding technique on actual microsystems chips.

Summary of Accomplishments:
This collaborative project between UTEP, UACJ (Universidad Autonoma de Ciudad Juarez), and Sandia studied and used reduced melting of nanopatterned silicon for microsystems for applications such as bonding of packaging surfaces. It was discovered that a more general and useful 3D morphological transformation of micropatterned silicon was possible for special annealing conditions. Experiments were systematically performed to replicate the reduced melting point and 3D morphological transformation. Sharp diamond-like shaped structures were patterned successfully using nanoimprint lithography on SOI wafers. During the project, an extensive research capability was created at UTEP and UACJ including dry etching, lithography, annealing, and design. Four students were supported; one masters and one baccalaureate student graduated during the period. One of the technical challenges of the project was understanding and creating the specialized conditions required to observe the melting and reshaping phenomena. Through systematic experimentation and review of the literature, we were able to determine that high-temperature (>960 °C) in an extremely pure ambient with hydrogen and free of oxygen or alternatively in a high vacuum ($<10^{-8}$ Torr) was crucial. To achieve this, a custom-heating chamber was created. Results were encouraging in terms of the purity required; however, the necessary temperature of at least 960 °C was not achieved initially. Challenges associated with creating the nano- and micro-patterned silicon and SOI wafers were surmounted. This project successfully created processes for nanopatterning of silicon via collaboration between UTEP, UACJ, and UT-Austin. Moreover, the micropatterning was collaboratively and successfully performed at UTEP and UACJ. Additional work was performed at UACJ on the design of chevron actuators including the fabrication of a lithography mask. The purpose of this work was to heat the chevron arms with electrical current to the desired temperatures of interest to induce rounding of the tubular arms.

Significance:
This research benefits our efforts to develop microsystem-based components for application to nuclear weapons and other security functions. The work is furthering the advancement of advanced microsystem packaging methodologies, in particular how we can achieve hermetic bonding of packages using significantly reduced temperatures during processing. Such environments will lessen the deleterious effects of high temperature processing on microdevices during the packaging stage.

Neural Correlates of Attention: Correlates of Decision-Making for Action
130823

Year 3 of 3
Principal Investigator: T. J. Shepodd

Project Purpose:
The environment with which most brain systems of humans and other animals are almost constantly confronted is complex and continuously changing, with each time step updating a potentially bewildering set of opportunities and demands for action. Far from the controlled, discrete trials used in most neurological and psychological investigations, behavior outside the laboratory environment is a seamless and continuous process of monitoring (and error correction) of ongoing action, and of evaluating persistence in a current activity with respect to opportunities to switch tasks as alternatives become available.

Prior work on frontopolar and prefrontal task switching use tasks within the same modality (e.g., view a stream of symbols on a screen and perform certain response mappings depending on task rules). However, in these "task switches" the effector is constant: only the mapping of visual symbols to a specific button used for response changes. In this task, subjects are choosing what kinds of future action decisions they want to perform, where they can control either which body part will act, or which direction they will orient an instructed body action. An effector choice task presents a single target and the subject selects which effector to use to reach the target (eye or hand). While the techniques available for humans can be less spatially resolved compared to non-human primate neural data, they do allow for experimentation on multiple brain areas with relative ease. Thus, such experiments address a broader network of areas involved in motor decisions.

In this project, we address a current dispute regarding the specific functional roles of brain areas that are often co-activated in studies of decision tasks, dorsal premotor cortex (PMd) and posterior parietal cortex (PPC). In one model, the PPC distinctly drives intentions for action selection, whereas PMd stimulation results in complex multi-joint movements without any awareness — nor subjective feeling of — having willed the elicited movement, and thus, the brain region seems to merely help execute the chosen action.

Summary of Accomplishments:
We conducted a study with fourteen healthy subjects (mean age 23.2 years, range 19-28; 5 females). All volunteers gave informed written consent before participation. All procedures were reviewed and approved by the California Institute of Technology Institutional Review Board (IRB). All volunteers were native English speakers, hand normal or corrected-to-normal vision, and right-handed. Electroencephalography (EEG) data were collected using a 128-channel HydroCel Geodesic Sensor Net with AgCl-plated electrodes in fitted sensor nets. Evoked brain potentials were digitized continuously at a sampling rate of 1000 Hz, filtered with 400-Hz low-pass and 0.1-Hz high-pass cutoff. Vertex electrode (Cz) served as reference during recording. Impedances for all channels were kept below 50 kV throughout the experiment, with adjustments during the breaks. Although readjustments could potentially affect signal quality across runs, slow voltage drifts associated with increased impedance minimally distort the averaged event-related potentials (ERP) and were cleaned from the data during artifact removal. Data processing is ongoing.

Significance:
This project supports Sandia's cognitive science mission by studying the fundamental science associated with the thought and decision process. The study seeks to identify those areas of the brain directly responsible for changes in the cerebral cortex during decision-making for action in the absence of external reward. Successful experiments would enhance our ability to relate thought to action, which, in turn, would enable enhanced detection systems, aid the warfighter and be a step towards self-controlled prosthetics/robotics.

Investigation of the Richtmyer-Meshkov Instability on a Multimode Interface
130826

Year 3 of 3
Principal Investigator: B. B. Cipiti

Project Purpose:
Inertial confinement fusion (ICF) is hampered by a hydrodynamic instability where any imperfection on the interface between the ablator and deuterium-tritium (DT) fuel is impulsively accelerated, resulting in mixing between the fuel and the ablator. The mixing can reduce the yield of the fuel and distort the converging shock wave, so that thermonuclear conditions are not reached. In ICF experiments, such as on the Z Machine at Sandia and at the National Ignition Facility (NIF) at Lawrence Livermore National Laboratory (LLNL), a thorough understanding of this instability is crucial to successful advancement of controlled nuclear fusion. This phenomenon is also important in stellar evolution behind a supernova and in the mixing of fuel and oxidizer in hypersonic vehicles. This instability, known as the Richtmyer-Meshkov instability, has been studied in shock tubes by observing the growth of the interface between a pair of gases. This project will advance the understanding of these phenomena by using a membraneless interface accelerated by a strong shock wave using the facilities at the University of Wisconsin-Madison Shock Tube Laboratory. We have modified the existing experiment to create a system that can impose a multimode amplitude spectrum on the initial condition. This type of interface would bear a closer resemblance to the broadband amplitude spectrum of actual interfaces in ICF problems. Using various planar laser diagnostic techniques, we are studying the growth of this interface after being accelerated by a shock wave. The growth of the mixing zone between the two gases will be compared to models and numerical simulations. In addition, Particle Image Velocity allows the study of velocity fields. These are used to investigate the fluctuating kinetic energy spectra and their dependence on the amplitude spectrum of the initial interface.

Summary of Accomplishments:
The Richtmyer-Meshkov instability (RMI) is experimentally investigated using several different initial conditions and with a range of diagnostics. First, a broadband initial condition is created using a shear layer between helium+acetone and argon. The post-shocked turbulent mixing is investigated using planar laser induced fluorescence (PLIF). The signature of turbulent mixing is present in the appearance of an inertial range in the mole fraction energy spectrum and the isotropy of the late-time dissipation structures. The distribution of the mole fraction values does not appear to transition to a homogeneous mixture, and it is possible that this effect may be slow to develop for the RMI. Second, the influence of the RMI on the kinetic energy spectrum is investigated using particle image velocimetry (PIV). The influence of the perturbation is visible relatively far from the interface when compared to the energy spectrum of an initially flat interface. Closer to the perturbation, an increase in the energy spectrum with time is observed and is possibly due to a cascade of energy from the large length scales of the perturbation. Finally, the single-mode perturbation growth rate is measured after reshock using a new high-speed imaging technique. This technique produced highly time-resolved interface position measurements. Simultaneous measurements at the spike and bubble location are used to compute a perturbation growth rate history. The growth rates from several experiments are compared to a new reshock growth rate model.

Significance:
The advancement of energy technology is one of the key missions of DOE. Fusion energy systems have been held back due to a number of engineering issues. Inertial confinement fusion faces a large challenge of withstanding the shock induced by the fusion ignition. This project seeks to gain new understanding in shock physics to allow for the design of advanced systems in the future.

Relating Polymer Dynamics to Molecular Packing
130827

Year 3 of 3
Principal Investigator: A. Frischknecht

Project Purpose:
In many instances, material performance is affected by dynamics at the molecular level with timescales commensurate with (or longer than) the duration of the material's application at the macroscopic level. For instance, the time necessary for the polymeric strings of a tennis racket to adjust to an applied force is orders of magnitude longer than the duration of the impact with a ball. The fraction of the racket's energy transferred to the ball as opposed to that dissipated as heat is the result of molecular level motions. Analogous behavior is found in tires (where energy dissipation results in a smoother ride) and plastic-bonded high explosives (where creep due to the polymer binder is on the timescale of years and will degrade performance).

Our goals in this project are to understand the interplay between molecular packing, nano- and micro-rheology, and macroscopic response of bulk polymeric materials leading to a predictive capability for the dynamic response of polymers undergoing deformation. Difficulties center on the large separation of time scales between atomic collisions (10^{-10}) sec and the macroscopic timescales (1 to 10^7) sec). Fast relaxation behavior at high temperature is mapped onto slow relaxations at low temperature. Our work centers on doing this using molecular dynamics simulations in a convincing, robust, and efficient manner.

We investigated polymers of varying molecular structures and track both short-time, high-frequency, atomic-level motion and long-time, low-frequency, macroscopic motion. We have recently focused on "driven simulation" techniques. Importantly, this approach permits the inherent structure of the potential energy landscape to be probed. It also permits nonlinear effects to be probed, which would relate the performance of a material to its stress history. Our goal is the development of new insights into the glass transition resulting from an exploration of the dynamic heat capacity of simple model polymers. This high-risk, high-potential R&D entails a collaboration with New Mexico Institute of Technology.

Summary of Accomplishments:
In predictions of the aging of a viscoelastic material, it is necessary, in one form or another, to have the spectrum of relaxation times of the material. This is often done with rheometry where the storage and loss shear moduli are measured. A complementary approach is the dynamic heat capacity measured with differential scanning calorimetry (DSC). Advantages of using the heat capacity include permitting much smaller samples (milligram amounts) and that it measures a dynamic response that is more directly tied to thermodynamic treatments of the glass transition. The computational modeling of the dynamic heat capacity undertaken in this project was the first effort of this type. The general procedure and some preliminary results were reported in the first project paper (*Journal of Chemical Physics,* 131, 104507, 2009). The application of this procedure to an important model of the glass transition was the subject of our second paper (*Journal of Chemical Physics,* 133, 064508, 2010). Many theories of the glass transition are based on a potential energy landscape approach. Our third paper in 2011 demonstrated how our analysis technique could be used as a direct probe of this landscape.

Significance:
This project benefits the DOE science mission and Sandia's national security mission by addressing the time/frequency rheological response of plastic-bonded high explosives (PBX). Although a small percentage of the whole, the polymer binder has a marked effect on properties. Understanding the

relationship between the molecular structure of the elastomer and its complex modulus (viscoelastic behavior) would, for example, permit aspects of the aging of PBX to be linked to the mechanical properties of the material.

Refereed Communications:

J.R. Brown and J.D. McCoy, "The Potential Energy Landscape Contribution to the Dynamic Heat Capacity," *Journal of Chemical Physics*, vol. 134, p. 194503, May 2011.

Hazard Analysis and Visualization of Dynamic Complex Systems
135790

Year 3 of 3
Principal Investigator: N. N. Brown

Project Purpose:
As modern systems become increasingly complex, the nature of accidents is changing and safety analysis methods that have worked well in the past are becoming less effective. Traditional approaches such as fault trees are commonly used to analyze anticipated component failures, but it has become more common to encounter unanticipated safety problems as well. The current focus on component failure also misses the most common causes of accidents in today's safety-critical systems. Dysfunctional and unanticipated interactions play an increasingly critical role in modern complex systems, but are easily overlooked by current safety methods. Software is particularly difficult to analyze with current methods because it does not fail in the way that hardware does or in the way assumed by most hazard analysis and risk assessment techniques. Human components are also difficult to analyze because they often interact with the system in complex ways that are not addressed by current failure-based accident models.

This project is developing a new safety analysis methodology in collaboration with Massachusetts Institute of Technology, which addresses not only traditional component failure accidents, but also accidents that arise from dysfunctional component interactions, software malfunctions, human error, design error, and other unanticipated problems. The STAMP (systems-theoretic accident modeling and processes) model of accident causation seeks to extend current "chain-of-events" techniques by using control theory to identify and mitigate hazards that emerge from both human and non-human component interactions rather than merely attempting to eliminate component failures (which are only one cause of hazards). Additional research is also necessary to refine the accident models, define a methodology that accommodates uncertainty and dynamics in complex systems, and to investigate ways of visualizing and illustrating the analysis results. This approach may be applicable to safety analyses of nuclear weapon design, production, and deployment systems. These problems are not currently being addressed by the Nuclear Weapons (NW) mission because there are no commercially available software tools to apply.

Summary of Accomplishments:
The first milestone for FY 2011 focused on more detailed models and methods within the STAMP framework to support the analysis of hazards in complex systems. STAMP-based hazard analysis (STPA) is based on the identification of unsafe control actions in a system that is then analyzed further to determine their causes. Although STPA has been successfully applied a few times in an ad-hoc manner by experts, the process of identifying unsafe control actions has thus far relied heavily on expert judgment because there was no systematic method to uncover these actions. However, in this project, a new view of unsafe control actions has been developed that integrates individual actions together with the relevant context. Based on this view, a systematic approach for identifying unsafe control actions has been defined and is currently being tested on real-world systems, including an unmanned cargo vehicle for the International Space Station, a medical proton therapy device, and a weather satellite.

The second milestone involved a comparison with other approaches. As mentioned above, the newly developed approach is currently being applied to a number of real-world systems that have previously been analyzed with other methods. So far, the results have been very promising — the new approach has identified all unsafe control actions that had been previously identified (for a given subsystem), in addition to several new unsafe control actions that had been previously overlooked.

Particularly promising are accomplishments beyond our project milestones. Because the new approach defines such a systematic process, there is the potential for automating much of the hazard analysis. In fact, given a few simple inputs from a human analyst, the corresponding safety constraints/requirements for the design can be automatically generated along with the control algorithms necessary (but not sufficient) to prevent the identified hazards.

Significance:
STPA, a new hazard analysis method, has been found to be more powerful than existing methods in that it incorporates additional causes of accidents in complex systems. However, it has only been applied in an ad-hoc manner and has been limited to unsafe behavior that was anticipated by the analyst. The new systematic process can, in theory, identify potentially hazardous behavior that was not previously anticipated, and in fact when applied to real-world systems, it uncovered a number of hazardous behaviors that had been overlooked by previous analyses.

This new approach is applicable to safety analyses in many different domains, including nuclear weapon design, production, and deployment systems. In addition, the new approach is designed to be applied during early phases of design. While current hazard analysis methods cannot be applied until late in the design process — when the cost to "make it safe" is most expensive — the new approach can be applied when the cost of change is minimal.

The new approach is also applicable not only to the technical parts of a system, but also to broader human and organizational components. The social and organizational effects of complex systems on safety are applicable to DOE's high-priority efforts in national security, including nuclear weapon security and safety analyses, cyber security protection, and operations security. Current analytical methods may be inadequate to reveal how modest changes to a system could add significant unrecognized vulnerabilities. Similarly, operational security is based on protection of isolated assets, and the interactions of these assets are not well understood. The social/organizational model developed in this project will be applicable to identify gaps in the structure that are vulnerabilities of the organization.

Processor Modeling for Use in Large-Scale Systems Models
137299

Year 3 of 3
Principal Investigator: E. DeBenedictis

Project Purpose:
The primary focus of this project is on development of stochastic processor and memory models that can be useful as stand-alone performance prediction tools and as components within a large-scale simulator, particularly Sandia's Structural Simulation Toolkit (SST). The breadth of this focus also includes work on integrating models into and enhancing them such that they are useful with SST.

A secondary focus of this project has developed in the broad area of workload characterization. In developing stochastic processor models, we collected benchmark performance data to be used as inputs to these models. Since this data is an artifact of the model development process, we are using it to do a performance analysis and workload characterization of Sandia's Mantevo MiniApps. The focus here is both on performance analysis and on MiniApp validation (ensuring that the MiniApp exhibits the same behavior at the architecture level as the original application).

Summary of Accomplishments:
In FY 2011, we have completed further development on the Opteron Monte Carlo processor model (MCPM), initially developed in collaboration with Presidential Early Career Award for Scientists and Engineers awardee, Dr. Jeanine Cook of New Mexico State University. Several enhancements have been made to increase accuracy, including an improved fetch mechanism, and a more accurate instruction decoder component. We are currently preparing a paper on the new model for submission to the International Conference on Performance Engineering (ICPE).

The Niagara I, Niagara II, and Opteron MCPM models have been re-integrated into SST. These models were originally developed to be used as a stand-alone tool for performance prediction. They were not developed and written to be integrated into a larger simulator such as SST since the models do not actually execute instructions and save results. Therefore, we have partially developed a functional front end for each of these models that will decode an incoming binary instruction, functionally execute the instruction, and produce results that are written to a register file. The functional front end for the Opteron model is currently being developed.

We have also been working on the performance characterization of the Sandia Mantevo MiniApps. We have developed several tools to collect dynamic performance data including data dependence distances, memory reference stride distribution, spatial and temporal locality of memory references and detailed instruction mix information. We are currently preparing a paper titled, "Quantitative Performance Comparison of Mantevo MiniApps and the SPEC CPU2006 Benchmark Suite on a Contemporary X86 Architecture," to be submitted to a conference call for papers (CFP) this fall.

We are also working to develop a simulator within SST to enable analysis of the performance of a local memory store to replace on-chip cache on multi-core processors. We are in the process of developing the front-end Instruction Set Architecture (ISA) decoder and a generic processor model in which we can model this new memory.

Significance:
Microarchitecture simulation applies to the design of high performance computers. These types of computers will be used by Advanced Simulation and Computing (ASC) and other DOE missions for

nuclear weapons simulation, extreme scalability initiatives for scientific research, in manufacturing facilities like Microsystems and Engineering Sciences Applications (MESA) and Center for Integrated Nanotechnologies (CINT), and for intelligence community problems, and space computing.

The Mantevo MiniApps are gaining widespread attention as a means to do fast performance prediction and analysis, algorithm development, simulation of next generation systems, and application understanding. They will play an important role in defining next-generation computational platforms important to ASC and key DOE missions.

Refereed Communications:

J. Cook, J.E. Cook, and W. Alkohlani, "A Statistical Performance Model of the Opteron Processor," *ACM Performance Evaluation Review*, vol. 38, March 2011.

A.F. Rodrígues, K.S. Hemmert, B.W. Barrett, C. Kersey, R. Oldfield, M. Weston, R. Risen, J. Cook, P. Rosenfeld, E. Cooper Balls, and B. Jacob, "The Structural Simulation Toolkit," in *Proceedings of the ACM Performance Evaluation Review*, pp. 37-42, 2011.

Responsive Nanocomposites
141076

Year 3 of 4
Principal Investigator: T. J. Boyle

Project Purpose:
The creation of environmentally responsive nanocomposites will yield materials with increased robustness and stability. To produce such nanocomposites requires that the surface interaction between functionalized nanoparticles and a given matrix be better understood and controlled. This project attacks this problem by invoking a multidisciplinary approach based on predictive computational models and experimental verification using a series of well-controlled complex nanomaterials dispersed in a variety of elastomeric or soft materials. We will determine the proper chemical species and length of the functional groups and the required surface coverage density of morphologically and compositionally varied nanomaterials dispersed in these matrices. A model for nanocomposite mixtures that possess "active" or "applied" responses to temperature or hydration environmental changes will be developed. Our initial response stimuli will focus on temperature or hydration since these are two of the major issues identified to be of interest to Sandia and our industrial partners. The project will be initiated by building on Sandia's expertise in the synthesis of tailored nanomaterials of varied compositions and functionalizations, nanocomposite self-assembly, and computational modeling of nanocomposites aided by several key university professors, students, and industrial partners with expertise in nanocomposite testing.

The production of responsive nanocomposites requires the development of fundamental concepts and data to understand the nature and theory of nanomaterials interaction with polymeric materials. The diverse nature of the project requires a multidisciplinary approach to investigate the understanding required to make the advances necessary to realize the goal of this project. This study will foster additional sponsors as progress is realized.

Summary of Accomplishments:
- Controlled photocatalytic growth of old triangles
- Platinum dendrites photocatalytically grown on nanocarbon
- Pt and Au grown on cooperative binary ionic (CBI) materials
- Generated a wide variety of nanoparticles
- Established baseline electrospinning processes of a variety of polymers
- Established a nanocomposite baseline for reactive polymers
- Developed responsive nanopolymer wires (PK, Sigmund)
- Developed pH-responsive membranes using poly-4-vinyl pyridine
- Demonstrated pH-dependent hydraulic permeability
- Demonstrated that a polymer can tunably reject solute particles
- Submitted "Direct Writing and Actuation of 3D-Patterned Hydrogel Pads on Micropillar Supports," recently accepted for publication in *Angewandte Chemie Int. Ed.*
- Developed a new method for patterning platinum and palladium with multiphoton lithography
- Developed a new aerosol through plasma (ATP) synthetic method for disordered graphenes
- Prepared a new UV-photo-responsive self-assembled reduced graphene oxide-TiO_2 nanometer films
- Prepared Au-TiO_2 core-shell nanoparticles (to extend photo-response to visible wavelengths)
- Prepared ferrocene-silane ligand (to develop light [or] electrical mediated responsive materials)
- Modeled amine terminated alkanethiol Au nanoparticles in water and decane
- Simulated the assembly of Au nanoparticles at a water/vapor interface

- Developed a methodology to extract forces between coated nanoparticles in a polymer matrix

Significance:
This project employs a multidisciplinary research group consisting of national laboratory and university personnel who are developing fundamental scientific theories and experimental results concerning responsive nanocomposites. It is expect that this effort will address a wide range DOE application, with an emphasis on energy-related needs. In addition, it is expected that these materials will address nuclear weapons–related issues. The students will be involved in every aspect of this project and based on this initial interaction may lead to identifying potential candidates for future DOE efforts.

Refereed Communications:
T.N. Lambert, C.A. Chávez, N.S. Bell, C.M. Washburn, D.R. Wheeler, and M.T. Brumbach, "Large Area Mosaic Films of Graphene-Titania: Self-Assembly at the Liquid-Air Interface and Photo-Responsive Behavior," *Nanoscale*, vol. 3, pp. 188-191, November 2010.

T.N. Lambert, C.C. Luhrs, C.A. Chávez, S. Wakeland, M.T. Brumbach, and T. M. Alam, "Graphite Oxide as a Precursor for the Synthesis of Disordered Graphenes using the Aerosol-Through-Plasma Method," *Carbon*, vol. 48, pp. 4081-4089, November 2010.

T.J. Boyle, L.A.M. Ottley, and S.M. Hoppe, "Series of Comparable Dinuclear Group 4 Neo-Pentoxide Precursors for Production of pH Dependent Group 4 Nanoceramic Morphologies," *Inorganic Chemistry*, vol. 49, pp. 10798-10808, December 2010.

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T.J. Boyle, L.M. Ottley, and R. Raymond, "Unusual Structurally Characterized Pyridine Carbinoxide Copper(II) Coordination Compounds, Isolated from Organic Solvents," *Journal of Coordination Chemistry*, vol. 63, pp. 545-557, 2010.

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T.J. Boyle, R. Raymond, D.M. Boye, L.M. Ottley, and P. Lu, "Structurally Characterized Luminescent Lanthanide Zinc Carboxylate Precursors for Ln-Zn-O Nanomaterials," *Dalton Transactions*, vol. 39, pp. 8050-8063, 2010.

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S.R. Challa, Y. Song, J.A. Shelnutt, J.E. Miller, and F. van Swol, "Evolution of Dendritic Nanosheets into Durable Holey Sheets: A Lattice Gas Simulation Study," *Journal of Porphyrins Phthalocyanines*, vol. 15, pp. 449-458, May 2011.

Y. Tian, K.E. Martin, J.Y. Shelnutt, L. Evans, T. Busani, J.E. Miller, C.J. Medforth, and J.A. Shelnutt, "Morphological Families of Self-Assembled Porphyrin Structures and their Photosensitization of Hydrogen Generation," *Chemical Communications*, vol. 47, pp. 6069-6071, April 2011.

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Nature Versus Nurture in Cellular Behavior and Disease
141704

Year 2 of 3
Principal Investigator: C. J. Brinker

Project Purpose:
This project is vigorously pursuing two complementary, interrelated goals: 1) the incorporation of individual or groups of bacterial, fungal, or mammalian cells within novel 3D cell-built or lithographically defined matrices that provide an engineered chemical and physical background to inform cells and direct their behavior and 2) the development of two classes of targeted nanoparticle delivery platforms, protocells (porous nanoparticle supported lipid bilayers) and virus-like particles (VLPs), which could be selected against dormant/drug resistant/metastatic cells and selectively deliver multicomponent cargos (cocktails) to this recalcitrant population. This project provides a unique means for understanding environmental influences on cellular behavior, in particular, dormancy, drug resistance, metastasis and nanoparticle toxicology. It will enable the development of new targeting and drug delivery strategies designed to selectively attack and kill dormant and drug resistant cells, thereby reducing a significant reservoir of human disease. It will establish the scientific basis for creating new classes of cell based sensors, and it will provide a platform in which to understand nanoparticle toxicology in 3D environments, which better represent in vivo conditions.

Summary of Accomplishments:
1. We adapted our tailorable hybrid bio/inorganic 3D matrices (*Science* 2006; *Nature Chem Biol*. 2010) to cancer hepatocarcinoma cells. Integrated cells are non-replicative and drug resistant but maintain biofunctions like protein production, pinocytosis, and receptor-mediated endocytosis. These dormant cell states are resistant to external threats and could serve as reporters of environmental/battlefield conditions or as autonomous factories for enzyme production.
2. Using multiphoton protein lithography, we fabricated arbitrary 3D biomolecular architectures with natural or non-natural structures but retained biomolecular activity and biocompatibility. Through grayscale control, the properties, (e.g., modulus and diffusivity) and activity of the resulting protein architectures were optically defined. Such structures serve as 3D micro-environmental chambers in which to study and direct cellular behavior at the individual cell and multicellular levels.
3. We showed the direct conversion of lithographically defined 3D protein scaffolds to silicon dioxide and their further transformation to silicon. This biomineralization process mimics features of diatom formation and results in a new class of rugged biocomposites with retained biofunctionality.
4. We discovered a generalized process, Silica Cell Replication, wherein mammalian cells direct their exact replication in silico. The silica cell replicas preserve nano to macroscale cellular features and dimensions after drying at room temperature. Re-exposure to water provides access to intracellular components, where preliminary experiments show retention of enzymatic activity.
5. We showed that the combined stability, cargo capacity, and targeting selectivity of protocells results in a million-time improvement in selective cytotoxicity to drug resistant hepatocarcinoma cancer cell lines compared to the corresponding FDA-approved liposomal delivery agent (*Nature Materials*, feature cover article, May 2011).
6. We demonstrated selective delivery of nanoparticles, chemotherapeutic drugs, siRNA cocktails, and protein toxins to human hepatocellular carcinoma with MS2 virus-like particles (*ACS Nano*, feature cover article July 2011).

Significance:
This project contributes substantially to Sandia's DOE nanoscience, DHS, and national security missions. Cellular integration within engineered 3D matrices will create new biotic/abiotic functional nanocomposites that could serve as ultrasensitive cell-based environmental sensors (DHS/National Security (NS)/Defense Threat Reduction Agency [DTRA]) or platforms for studying and directing behavior at the individual cell level, relevant to immune response and outbreak of disease (DHS/NS). Protocells and VLPs represent two breakthrough multifunctional nanoparticle systems important for drug delivery, imaging, and ultrasensitive sensors of arbitrary targets (DHS/NS). Our research has led to extramural research grants with the National Institutes of Health (NIH), National Cancer Institute (NCI), and National Science Foundation (NSF), as follows:

- NIH Award 1 R01 GM098736-01 (Brinker, Jakobssen, Maloy, Sandia/University of New Mexico (UNM), University of Illinois at Urbana-Champaign (UIUC), San Diego State) — "Genetically Specific Therapy against Pathogenic Bacteria."

- NIH NCI Award 1 U01 CA151792-01 (Brinker and Willman, Sandia/UNM)— "Peptide-Directed Protocells and Virus-Like Particles — New Nanoparticle Platforms for Targeted Cellular Delivery of Multicomponent Cargos."

- National Institute of Environmental (NIEHS) Award 1 U19ES019528-01 (Andre Nel, UCLA) Center for Nanobiology and Predictive Toxicology

- NSF:ERC 0830117 (Andre Nel, UCLA) Center for Environmental Implications of Nanotechnology (CEIN)

Additionally, based on our protocell nanoparticle delivery platform, we were also invited to present at the DTRA workshop on a "SMART-DDS" (Sensing, Multi-Phased, Aimed, Responding Transport (SMART) - Drug Delivery Systems) platform technology, August 2-5, 2011, Springfield, VA.

Refereed Communications:
L.D. Zarzar, P. Kim, M. Kolle, C.J. Brinker, and B.J. Kaehr, "Direct Writing and Actuation of Three-Dimensionally Patterned Hydrogel Pads on Micropillar Supports," *Angewandte Chemie*, vol. 50, pp. 9356-9360, September 2011.

C.Y. Khripin, D. Pristinski, D.R. Dunphy, C.J. Brinker, and B.J. Kaehr, "Protein-Directed Assembly of Arbitrary Three-Dimensional Nanoporous Silica Architectures," *ACS Nano*, vol. 5, pp. 1401-1409, January 2011.

H.K. Baca, E.C. Carnes, C.E. Ashley, D.M. López, C.M. Douthit, S. Karlin, and C.J. Brinker, "Cell-Directed-Assembly: Directing the Formation of Nano/Bio Interfaces and Architectures with Living Cells," *Biochimica et Biophysica Acta,* vol. 1810, pp. 259-267, March 2011.

C.E. Ashley, D.R. Dunphy, Z. Jiang, E.C. Carnes, Z. Yuan, D.N. Petsev, P.B. Atanassov, O.D. Velev, M. Sprung, J. Wang, D.S. Peabody, and C.J. Brinker, "Convective Assembly of 2D Lattices of Virus-Like Particles Visualized by In-Situ Grazing-Incidence Small-Angle X-Ray Scattering," *Small*, vol. 7, pp. 1043-1050, April 2011.

C.E. Ashley, E.C. Carnes, G.K. Phillips, D. Padilla, P.N. Durfee, P.A. Brown, T.N. Hanna, J. Liu, B. Phillips, M.B. Carter, N.J. Carroll, X. Jiang, D.R. Dunphy, C.L. Willman, D.N. Petsev, D.G. Evans, A.N. Parikh, B. Chackerian, W. Wharton, D.S. Peabody, and C.J. Brinker, “The Targeted Delivery of Multicomponent Cargos to Cancer Cells by Nanoporous Particle-Supported Lipid Bilayers,” *Nature Materials*, vol. 10, pp. 389-397, April 2011.

CE. Ashley, E.C. Carnes, G.K. Phillips, P.N. Durfee, M.D. Buley, C.A. Lino, D.P. Padilla, B. Phillips, M.B. Carter, C.L. Willman, C.J. Brinker, J.C. Caldeira, B. Chackerian, W. Wharton, and D. S. Peabody, “Cell-Specific Delivery of Diverse Cargos by Bacteriophage MS2 Virus-Like Particles,” *ACS Nano*, vol. 5, pp. 5729-5745, July 2011.

Understanding the Fundamentals of Plastic Deformation
141712

Year 2 of 3
Principal Investigator: C. R. Weinberger

Project Purpose:
This project investigates a few fundamental aspects of plasticity at the micro- and nanoscale: dislocation motion and multiplication, dislocation nucleation, and homogenization of dislocation structures.

Dislocation motion in small volumes is complicated because of the high surface to volume ratio in these structures. Much of the research so far has concentrated on how the free surfaces give rise to additional forces and the annihilation of dislocations at the surface. However, additional effects of free surfaces are less well known.

Similarly, the nucleation of dislocations from free surfaces, which is important in nanomechanics, depends on a variety of factors including loading direction, surface orientation, and the surface topology. The strength of nanomaterials is controlled by dislocation nucleation from surfaces and, therefore, models of this are greatly needed. Furthermore, there is a lack of comparisons with the emerging experimental evidence that is naturally more complicated.

Homogenization of dislocation structures is difficult because the connection between the overlying mechanical properties and the material microstructure is not well understood and may also depend on the loading conditions. This project aims at identifying important variables that describe the dislocation structure evolution using dislocation dynamics, which can help predict mechanical properties.

Connecting mechanical properties to material microstructure has been an overarching goal of material science since its inception. This project attempts to connect mechanical properties to the microstructure through the mechanics of dislocations. This is a high-risk project because it is not known if such general laws exist or how to formulate them. However, should the goals be met, this project has a great potential impact in many areas of mechanics of materials, significantly advancing our understanding of microstructure's role in material strength. The project PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments:
The project's first milestone, which has been completed, dealt with dislocation motion in small volumes. We completed a second study in this area that dealt with the stability of single arm sources in nanopillars. Single arm sources, or truncated Frank-Read sources, are believed to be one of the main contributors to plastic deformation in small volumes. However, the range of crystal sizes in which they operate and the pinning mechanisms are still not known. We have shown that Lomer-Cottrell jogs, which are hypothesized to be very stable and a candidate pinning point for single arm sources, are not stable. During the rotation of the single arm sources, the jog becomes mobile, making the source mobile and unstable. This result suggests that our understanding of the nature of pinning points is lacking and that more fundamental molecular dynamics simulations are needed to characterize the stability of dislocation pinning points.

For dislocation nucleation, we have recently completed a comprehensive study of the strength of gold nanowires, which is dominated by dislocation nucleation. This study uses a chain-of-states method in atomistics to determine the energy barriers to dislocation nucleation. Transition state theory is then used to estimate the strength of the nanowires at experimentally relevant temperatures and strain rates, which can now be directly compared with emerging experimental results. These atomistic simulations were augmented with continuum modeling of the energy barriers using the orientation-dependent line energy. The combination of methods shows that dislocations generally prefer to nucleate as a screw dislocation to reduce their energy. These results also show that square prisms are generally weaker than circular prisms because the line length of the dislocation is reduced in the corners of square pillars.

Significance:
Sandia's success relies on being at the forefront of materials characterization, modeling, and development. This work will provide improved fundamental basis for the development of materials models for the full range of missions at the Laboratories. Specifically, it addresses the problems of modeling material mechanical properties at the small scale and these developments are important for interpreting small-scale mechanical measurements and comparisons.

Refereed Communications:
C.R. Weinberger and W. Cai, "The Stability of Lomer-Cottrell Jogs in Nanopillars," *Scripta Materialia*, vol. 64, pp. 529–532, March 2011.

C.R. Weinberger, "The Structure and Energetics of, and the Plasticity Caused by, Eshelby Dislocations," *International Journal of Plasticity*, vol. 27, pp. 1391-1408, September 2011.

Development of First-Principles Methodologies to Study Electro-Catalytic Reactions at Metal/Electrolyte Interfaces
141927

Year 2 of 3
Principal Investigator: B. Debusschere

Project Purpose:
Electrochemical processes occurring at metal/electrolyte interfaces are the basis of many devices facilitating conversion between different forms of energy such as solar, electrical, and chemical. For example, fuel cells, electrolyzers, and batteries are used for conversion between chemical and electrical energy. While these devices vary widely in the specifics of operating conditions, materials composition, and energy input, their performance is, to a large degree, governed by similar molecular electrochemical transformations involving transfer of charged species across metal/electrolyte interfaces. These critical electrochemical transformations are poorly understood and difficult to probe with conventional experimental tools because the metal/electrolyte interfaces are hidden and inaccessible to the experimental probes.

To address these issues, this joint project with the University of Michigan employs quantum Density Functional Theory (DFT) calculations and kinetic Monte Carlo (KMC) simulations defined from ab initio methods to study elementary step mechanisms of electrocatalytic reactions in electrochemical devices. Realistic model systems are employed that account for the presence of the metal/electrolyte interface. Potential bias and electric field effects are incorporated in the first principles calculations. The case study focuses, in particular, on the underlying electrochemical transformations governing the processes of oxygen reduction reaction (ORR) and H_2O electrolysis at metal/electrolyte interfaces, but the developed methodology is universal and can be easily employed to address other electrocatalytic systems where electrolyte/metal interface electrochemistry plays a role, such as solid-state sensors, microelectronic devices, solid-state batteries, fuel cells and many others.

The employed theoretical framework delivers molecular information that is virtually impossible to obtain through other means. The project will, on one hand, advance the ability to model molecular electrochemical transformation from first principles; and on the other hand, provide molecular information that is critical for the formulation of superior new materials for electrochemical transformations, including materials for fuel cells, electrolyzers, and batteries.

Summary of Accomplishments:
Building on our very general framework for studying electrochemical transformations at solid/electrolyte interfaces, developed in FY 2010, we continued our analysis of the oxygen evolution/reduction reactions in lithium/oxygen batteries.

The largest barrier to lithium/oxygen battery technology is associated with the loss of capacity post-recharge. The charging potential for the oxygen evolution reaction (Li-OER) is another major source of inefficiency in these batteries. Our analysis, therefore, focuses on this reaction, but our approach also describes the Li-ORR during discharging. Preliminary DFT calculations identified a few materials such as gold, platinum, and silver that bind oxygen weakly enough to be catalytically active towards oxygen evolution from lithium/oxygen compounds. Recent studies have suggested that carbonate-containing solvents participate in reactions, generate undesired side products, and reduce battery longevity through capacity loss. We demonstrated the effects of solvent on the Li-OER over gold and platinum surfaces, showing significant interaction between a model solvent, CO_3 and lithium/oxygen species on the surface. This captured the interaction between these adsorbed species and an organic carbonate solvent, the type used extensively in lithium-oxygen batteries for its polar properties and ability to dissolve discharge products. The interaction was more pronounced for platinum than for gold, suggesting that platinum electrode-based batteries are more sensitive to solvent interactions and performance degradation. The over-potential losses predicted for platinum and gold by these calculations were about 0.8 V. This compares reasonably well to experimental values that show over-potentials of no less than 0.7 V to 0.9 V. These calculations provide one strategy for potentially designing a catalyst with improved performance using carbonate-containing solvents: a catalyst design which inhibits the formation of carbonate-containing species could prove to lower over-potential losses and improve the stability of the battery through numerous charge and discharge cycles.

Significance:

While we focused on two particular electrochemical systems, the developed methodological framework is universal, and can be easily employed to address other electrocatalytic systems where electrolyte/metal interfaces electrochemistry plays a role, such as solid-state sensors, microelectronic devices, solid-state batteries, fuel cells and many others. By advancing our ability to model molecular electrochemical transformations from first principles, our methods can provide molecular information that is critical for the formulation of superior new materials for a wide range of electrochemical transformations. We anticipate these advancements will allow us to discover and engineer novel materials for electrochemical conversion through more systematic knowledge-based approaches, rather than empirical trial-and-error experimental approaches. This will have a direct impact on improving the performance of energy storage and conversion devices such as fuel cells, batteries, and electrolyzers. The improved performance of these devices is important in renewable energy production of variable renewable resources such as wind and solar, which need an energy reservoir to manage energy and provide constantly supplied power. This supports the DOE missions in terms of better science, predictive science-based design driving improved energy efficiency, reduced pollution, and renewable energy technologies. Improved energy efficiency also enhances our national security by lowering dependence on foreign oil. This supports DOE’s national security goal by reducing the dependence on fossil fuels and reducing the impact of energy use on climate change.

Covalently Cross-Linked Diels-Alder Polymer Networks
141928

Year 2 of 2
Principal Investigator: B. J. Anderson

Project Purpose:
This project examines the utility of cycloaddition reactions for the synthesis of polymer networks. Cycloaddition reactions are desirable because they produce no unwanted side reactions or small molecules, allowing for the formation of high molecular weight species and glassy crosslinked networks. Both the Diels–Alder reaction and the copper-catalyzed azide–alkyne cycloaddition (CuAAC) were studied. This work was performed in collaboration with the University of Colorado-Boulder. Accomplishments include new methods offering the promise of efficiently creating robust, high molecular weight species and delicate 3D structures that incorporate chemical functionality in the patterned material.

Summary of Accomplishments:
Our accomplishments encompassed three areas: 1) externally triggered healing of a thermoreversible covalent network via self-limited hysteresis heating, 2) Diels-Alder based photoresists, and 3) investigation of the photochemical catalysis of copper catalyzed azide–alkyne cycloaddition. In area 1, we had previously synthesized a reversibly crosslinked polymer network using the Diels–Alder reaction and demonstrated that, upon heating, the material readily reverted to a liquid composed of the initial monomers. While this material showed promise as a thermo-reversible adhesive and a self-healing material, remotely and rapidly heating optically thick and thermally sensitive materials is a nontrivial problem. Hysteresis heating, a process where an alternating magnetic field is used to heat magnetically susceptible materials, was evaluated as a method for heating, depolymerizing, and healing the material. Ultimately, we thereby demonstrated that the material could be fractured and healed at least ten times with no change in either the modulus or ultimate strength. In area 2, using Diels–Alder based polymer networks, we developed a photoresist based on the selective elimination of bond reversibility, and demonstrated its utility in 3D microstereolithography. Specifically, a thermoreversible crosslinked polymer network is formed by a Diels–Alder reaction between furan and maleimide-based monomers. Thiol and photoinitiating species are readily incorporated into the initial mixture, and upon irradiation, the Diels–Alder adduct undergoes a thiol-ene reaction, rendering the bond irreversible. Release of the patterned structure in the exposed region is achieved by reversion of the remaining reversible crosslinks to monomer via the retro Diels–Alder reaction. In area 3, initial rate experiments were performed to gain an understanding of the reaction mechanism. These results suggest that the CuAAC reaction is likely to be the rate-determining step under many experimental conditions, and undesirable side reactions of Cu(I) such as disproportionation, reduction of Cu(I) by radicals, and the reaction of Cu(I) with oxygen are avoided, likely by ligand protection.

Significance:
The project benefits the DOE science mission and national security by developing covalently crosslinked polymer networks that can be used in a variety of nuclear weapons, defense systems, and energy applications. Further, the research initiated the process of developing a fundamental understanding of the materials properties and of the aging behavior in relevant environments. This will be critical to advancing the technology readiness level (TRL) of these polymer systems so they can be applied to DOE missions. Since the W76-1 uses removable epoxy foam (REF) encapsulants and removable conformal coating (RCC) materials based on Diels-Alder chemistry, this work has direct nuclear weapons relevance.

Effect of Doping on the Performance of Solid-Oxide Fuel Cell Electrolytes Produced by a Combination of Suspension Plasma Spray and Very Low Pressure Plasma Spray
141929

Year 2 of 3
Principal Investigator: A. C. Hall

Project Purpose:
Plasma spray coating techniques allow unique control of electrolyte microstructures and properties. This can enable significantly improved solid oxide fuel (SOFC) designs. However, electrolytes deposited using conventional plasma spray have high porosities and cannot be applied in thin layers (< 50 µm). A solution to forming thin, dense electrolytes of ideal composition for SOFCs is being explored by combining suspension plasma spray (SPS), a new spray technique being developed by Purdue University, with very low pressure plasma spray (VLPPS) equipment available at Sandia's Thermal Spray Research Laboratory (TSRL). SPS feeds a suspension of very small powders within a solvent into the plasma. The solvent is evaporated, and the powders are melted or vaporized and propelled toward a substrate. Liquid- and vapor-phase deposition of the feedstock forms the coating (i.e., the electrolyte for this application).

Oxygen ion conductivity can be optimized using suspension plasma spray. It has recently been shown that dopant compounds dissolved in the suspension are incorporated into the coating during plasma spraying. Thus, it is possible to change the chemistry of the powder during the millisecond time the powder/dopant mixture is in the hot spray plume. Hence, it is now possible to quickly and systematically change the composition of the sprayed SOFC electrolyte to optimize its oxygen-ion conductivity by simply adjusting the suspension composition. SPS will, therefore, allow this project to systematically explore electrolyte doping and its influence on the performance of an SOFC system. Once the doped suspension is plasma sprayed, the electrolyte/coating will be characterized at Purdue as part of an SOFC system.

Summary of Accomplishments:
The feasibility of the combined suspension plasma spray (SPS) and very low-pressure plasma spray (VLPPS) coating process has been demonstrated by preparing thin, dense electrolyte coatings, and scandium doped electrolyte coatings. In addition, an SOFC test rig has been fabricated and used to evaluate electrolyte performance. The SPS/VLPPS process consistently produced well-adhered coatings 5–10 µm thick. SOFC test results show improved performance with scandium doping of yttria-stabilized zirconia (YSZ) relative to the un-doped YSZ. Various process parameters have been explored — including plasma torch power, chamber pressure, substrate temperature, standoff distance, dopant concentration, spray time, and powder loading. We added a remote operated in-situ ethanol flushing system that improved Sandia's SPS feed system. This allowed for increased spray time, efficiency, and reliability.

The effects of standoff distance, powder loading, spray time, and dopant concentration on the microstructure of SPS/VLPPS coatings have been investigated. The effect of standoff distance on electrolyte coating thickness was shown to be negligible within the tested range 43"–49", while surface roughness of the coating was seen as the limiting factor on the minimum achievable coating thickness. The effect of powder loading on electrolyte coating thickness showed a clear trend that can be approximated as ~(1.1 µm/min)*vol.%.

The fuel cell testing of the electrolyte coatings have shown improvement with Sc doping; however, a flaw in the testing has resulted in low current densities, negating the impact of these results. A standard fuel cell was purchased from Fuel Cell Materials, Inc. in an effort to compare results, given this limitation and as a method to clarify the testing flaw.

Significance:
This project will advance Sandia's capability in the area of VLPPS. VLPPS coating technology is an emerging coating technology that can prepare coatings in thickness/density regimes not currently accessible with conventional thermal spray or thin film processes. Improved ability to effectively prepare dense coatings in the 1 – 100 micron thickness regime with a wide range of compositions also allows for new coating solutions to be realized for broad-based application across DOE mission space including work associated with nuclear weapons, energy, and national security missions, as well as support of other federal agencies.

The specific focus of this coating project on SOFC electrolytes has the potential to significantly improve SOFC performance and efficiency, thus directly impacting Sandia's mission to develop improved energy technologies. Despite success developing SOFCs in the past 15-plus years, there is still need for improvement of current SOFC technology, particularly electrolyte materials. The ideal electrolyte is: 1) applied easily to non-planar shapes to take advantages of tubular SOFC designs, 2) both dense and thin (<50 μm), and 3) has optimized oxygen ion conductivity. Plasma spray coating techniques are a very promising way to prepare electrolytes on complex surfaces, thus satisfying criterion 1. However, conventional plasma-deposited coatings have high porosities and cannot be applied in thin layers (<50 μm) suitable for electrolytes. Also, control of the electrolyte composition is limited to the composition of the plasma spray feedstock powders.

By combining SPS with VLPPS, thin and dense electrolytes of ideal composition for SOFCs are possible. SPS feeds a suspension of nominally micron-sized powders within a solvent into the plasma. The solvent is evaporated, and the powders are melted and propelled toward a substrate. By working at pressures as low as 2.4 Torr, energy partitioning in the plasma and its interaction with the surrounding chamber atmosphere is dramatically reduced. The result is a significant increase in plasma mean free path length and plasma velocity. This causes the plasma to remain coherent longer and deposit uniformly over larger areas. It also increases the total time particles are entrained in the plasma, and consequently, the amount of energy these particles absorb. The increased residence time in the plasma ensures dopants diffuse into the powder before reaching the substrate. It has been shown that other compounds dissolved in the suspension (i.e., dopants) are incorporated into the coating during plasma spraying.

Thus, it is possible to change the chemistry of the micron-sized powder during the short millisecond time the powder/dopant is in the hot spray plume. This means that it is now possible to quickly and systematically change the composition of the sprayed SOFC electrolyte to optimize its oxygen-ion conductivity by simply adjusting the suspension composition. SPS, therefore, grants the ability to compositionally design electrolytes that maximize their performance as part of an SOFC system. This coating control capability has the potential to significantly improve the state of the art in SOFC electrolyte production and efficiency.

Quantum Enhanced Technologies (QET)
141930

Year 2 of 3
Principal Investigator: G. Biedermann

Project Purpose:
Quantum effects have a wide variety of applications in computation, communication, and metrology. We have experimentally investigated quantum-enhanced communications in the form of a quantum repeater for long distance quantum communication. We determined that such a system is within our current capabilities using neutral atom chips and Si microfabricated mirrors. To further explore practical quantum enhanced technologies, we are investigating quantum metrology in neutral atom systems. We believe this is a more fruitful path with near-term applications. The typical lower noise boundary on measurements of a two-level quantum system is given by quantum projection noise. This limits the signal-to-noise ratio (SNR) to SNR = sqrt(N) where N is the number of atoms. However, using the technique of spin squeezing, it has been demonstrated that one may increases uncertainty in one spin quadrature in exchange for decreasing uncertainty in another metrologically relevant quadrature, to result in SNR = N, which is known as the Heisenberg limit. This can deliver tremendous gains for typical systems that use $N = 10^4$ to 10^7 atoms. However, to realize the gains of quantum-enhanced metrology, one must first realize high-fidelity measurements of quantum systems. This fidelity is often limited by sources of technical noise in the system which must be characterized and mitigated. This work is done in collaboration with the University of New Mexico.

Summary of Accomplishments:
We analyzed performance of a microwave interferometer in $\sim 10^5$ Rb87 atoms, trapped in a magneto-optical trap (MOT). Initial results demonstrated poor SNR for large interrogation times (T = 3 ms) with the SNR limited to 20% of the Heisenberg limit, after correcting for the current state preparation scheme. Improvements were made to the apparatus, including magnetic shielding and modifications to the detection system. These modifications have brought us to within 80% of the Heisenberg limit. Primary limitations to this performance have been identified and are being corrected.

Finally, we conducted theoretical studies on using stimulated Raman transitions in the current apparatus. In particular, we studied the relationship between pulse efficiency and enhanced sensitivity through multipulse techniques. The primary SNR limitations were the temperature of the cloud, fringing of the laser beams, and phase noise of the lasers. The first two of these limit pulse efficiencies, which is a hindrance to techniques that enhance sensitivity through multiple pulses. For example, we found that a pi-pulse efficiency of 76% is required before any enhancement may be realized. Unfortunately, the fringing of laser beams results in an efficiency below this threshold. This limitation resulted in a redesign of the experimental apparatus.

Significance:
Enhancements from quantum metrology may be applied to two-level systems which are known for their exceptional performance in inertial sensing, clocks, metrology, and spectroscopy. As a specific example, accurate inertial measurements are essential in a region where global positioning systems (GPS) may be denied. Furthermore, these may be used for surveillance and reconnaissance, characterization of underground facilities, characterization for defeat, navigation of unmanned platforms, prompt global strike, and precision conventional munitions delivery. Precision navigation also relies on high performance time keeping in compact packages. The ultimate performance of such technology requires understanding sources of noise and mitigating them to reach the Heisenberg limit.

Remote Sensing Using Optical Filaments
141931

Year 2 of 3
Principal Investigator: M. Pack

Project Purpose:
Remote sensing of clouds using optical radiation (i.e., lasers) is a relatively mature research field, but there are significant fundamental questions that remain to be answered. For example, how well can two clouds containing different particles be differentiated using parameters such as depolarization ratios and their variations as a function of angle. The fast accurate modeling of cloud scattering plays a vital role in answering these questions.

One promising method of calculating radiative transfer for plane-parallel layers is the multicomponent approach (MCA). The MCA is a semi-analytic small-angle scattering approximation. What makes the MCA different from other approaches is that the small angle scattering component can be solved very efficiently using an analytic solution given in the previous publications; indeed, it exhibits incredible advantages in terms of computational time and exhibits comparable accuracy when pitted against more conventional methods.

In this project, we are developing an MCA program for the scalar radiative transfer equation, and to build on this code in order to calculate the full Stokes parameterization of scattered radiation. We will then take the method to the next level and include the k-distribution method and other modern developments.

This code will allow us to calculate the internal field structure of particles in clouds that will lead to a better understanding of both fluorescence and Raman scattering. A potential side benefit is that this research could provide insights into bio-inspired materials by aiding in the understanding of how cephalopods use chromatophores and iridophores for camouflage. The work is in collaboration with Texas A&M University.

Summary of Accomplishments:
This year, we have completed several projects relating to femtosecond laser pulse filamentation. We have studied the nonlinear effects involved between intersecting laser filaments in bulk liquids and have identified a previously unreported phenomenon involving energy transfer between filaments that occurs on the scale of the optical period of the incident laser pulse. We have also developed a method of imaging remote objects using filaments that results in an image resolution finer than the diffraction limit will allow. In addition to this, we have presented our experimental findings at various international conferences.

Significance:
The propagation of electromagnetic radiation and its scattering in turbid media are extremely relevant to Sandia mission areas in homeland security, defense systems and assessments (DSA), and nonproliferation because this physics determines the functionality and sensitivity of many remote sensing instruments. For example, laser remote sensing and spectroscopy play significant roles in gathering information about large and often inaccessible areas quickly providing the information necessary to make quick and accurate decisions.

Modeling and Simulation of Explosive Dispersal of Liquids
141932

Year 2 of 3
Principal Investigator: A. Brown

Project Purpose:
Explosive dispersal of liquids is a problem of great interest to national defense and security. For example, rapid dispersal of liquid fuel by an initial central burster charge and subsequent detonation of the resulting fuel-air mixture has been recognized to offer much higher damage potential than conventional warheads. On the other hand, in order to contain the potential damage created by an explosive charge set off in chlorine or a liquid fertilizer tank, it is important to be able to predict the resulting extent, timescale, and pattern of dispersal. In these scenarios, the liquid is initially propelled outward, either as liquid sheets through cracks that have been initiated in the container, or as an outward propagating liquid shell if the container is entirely fragmented, or a combination of the two. The outward expansion of the product of initial detonation rapidly accelerates these liquid sheets. A complex sequence of Rayleigh-Taylor, Richtmyer-Meshov and other secondary instability mechanisms follow that shred the liquid jets and sheets into a dispersion of tiny droplets. The problem of liquid dispersal can thus be separated into a near-field and a far-field regime, where the initial ejection of the liquid and its evolution to a fine mist of droplets will be termed near-field. The subsequent evolution of the droplets and their interaction with the ambient air and the detonation products will be termed far-field. In collaboration with the University of Florida, we are pursuing detailed hydrodynamic modeling and simulation of the initial ejection of the liquid, its subsequent break-up process and the final far-field dispersion of the liquid droplets. A combination of stability analysis, population balance, and large-scale scientific simulations are used to address this problem.

Summary of Accomplishments:
The shock physics code at University of Florida was modified and tested for inviscid shocks and for modal formation from rapidly propagating shock waves. Fundamental testing revealed the formation of dominant modes from the system of Eigen solutions. Three papers were written this year — two conference papers submitted and accepted to conferences, and a paper submitted to the Journal, *Physics of Fluids*.

Significance:
This research will enhance our fundamental understanding in a problem of great importance to national defense and security, in terms of the increased effectiveness of new types of warheads, and also strategies to mitigate the destructiveness of certain types of adversary weapons. This problem is of immediate relevance and interest to Sandia, DOE, DoD and the Defense Threat Reduction Agency (DTRA).

MBE Growth and Transport Properties of Carbon-Doped High Mobility Two-Dimensional Hole Systems
141933

Year 2 of 3
Principal Investigator: J. L. Reno

Project Purpose:
This project involves the study of molecular beam epitaxy (MBE) growth, device fabrication, and transport properties of 2D hole systems in carbon doped GaAs heterostructures. This research will be of interest to a wide audience of individuals in physics, electrical engineering, and materials science because this research involves fundamental research in materials growth, novel devices in electronics and spintronics, and low-dimensional systems for use in fundamental physics research. Specifically, we will research carbon doping in MBE grown GaAs films as a function of new cell design and architecture. The initial stages of the work will center on characterization and optimization of these thin-film materials with a new generation of GaAs system at Purdue University's Brick Nanotechnology Center. After the characterization is completed, these films will be used to fabricate devices for low-temperature transport measurements. The results of this study are expected to guide the development of future Sandia GaAs MBE systems for efforts such as quantum computing and terahertz sensing, both of which rely on high-mobility structures. In this effort, Sandia is leveraging the GaAs MBE capabilities at Purdue University to provide a testbed for new system designs and high-mobility GaAs film deposition techniques

Summary of Accomplishments:
We are now able to produce 2-dimensional electron systems (2DESs) and 2D hole systems (2DHSs) that display fraction quantum Hall effect (FQHE) physics that is among the best in the world. After finishing the installation of our machine, initial machine calibration growths began at the beginning of the calendar year and, by the end of February, we were able to achieve an electron mobility of 1.5×10^6 cm^2/Vs at liquid helium temperatures. Progress over the intervening few months has been rapid with peak electron mobilities of 15×10^6 cm^2/Vs at T = 300 mK and peak hole mobilities of 2×10^6 cm^2/Vs at T = 50 mK and density 6.2×10^{10} $cm^{-2.}$ The hole mobility, in particular, is impressive in that it is comparable to the highest quality samples reported in the literature at this density. In addition to our growth efforts, we have completed analysis with the help of collaborators of transport measurements made on an extremely high-mobility hole sample grown at Bell Laboratories. This analysis indicates that, in hole systems, the low temperature transport characteristics can be dominated by effects that are negligible in electron systems of similar carrier density. This result is clear evidence that there is still much to be understood about 2DHSs and underlines the importance of this research to further advance the state-of-the-art in 2DHSs. We are publishing these results in *Physical Review B*.

Significance:
This research is well aligned with the DOE's mission of advancing basic science in support of national security through missions such as quantum computing and terahertz sensing. In addition, the high-mobility GaAs film deposition techniques developed herein can be used to guide the development of future Sandia's MBE systems.

Refereed Communications:

J.D. Watson, S. Mondal, G.A. Csathy, M.J. Manfra, E.H. Hwang, S. Das Sarma, L.N. Pfeiffer, and K.W. West, "Scattering Mechanisms in a High-Mobility Low-Density Carbon-Doped (100) GaAs Two-Dimensional Hole System," *Physical Review B*, vol. 83, p. 241305, June 2011.

Power Reduction Techniques for Modern Modulation Schemes
142044

Year 2 of 3
Principal Investigator: R. J. Punnoose

Project Purpose:
This project has focused on Peak-to-Average Power Ratio (PAPR) reduction and its efficient and practical implementation for orthogonal frequency division multiplexing (OFDM) data transmission. There are many challenges and opportunities in increasing spectral and power efficiency in modern wireless digital communication systems. OFDM is a popular and effective way to send high-data-rate transmissions with high spectral efficiency, and its use has been included in many wireless standards such as WiMax, LTE, and DVB-T. A problem we address in this work is OFDM's high PAPR, which when reduced, leads to power savings at wireless transmitters. A method for PAPR reduction without requiring excess bandwidth has been developed and is being generalized to orthogonal frequency division multiplexing access (OFDMA) and multiple-input and multiple-output (MIMO) OFDM. In addition, lower complexity solution techniques that trade off performance for the capacity to handle larger OFDM frames are being investigated. Finally, related problems in OFDM such as finite alphabet effects for precoded OFDM are also being considered. This work is in collaboration with the University of California at Davis (UC-Davis).

Summary of Accomplishments:
The investigation of PAPR reduction for OFDM has yielded many results this past year. An IEEE conference paper, "A Convex Optimization Approach to Reducing Peak-to-Average-Power Ratio in OFDM," was presented in May 2011 at the Institute of Electrical and Electronics Engineers (IEEE) International Symposium on Circuits and Systems (ISCAS) Conference in Rio de Janeiro. That paper summarizes results from the 2009-2010 year, but also contains new analysis on actual power savings at the power amplifier.

In our survey of PAPR reduction-related works, we found these kind of practical results were uncommon. After consultation with an expert and author in this area, we were able to get data on power amplifiers and characterize the actual power saving abilities of this work. We also investigated using techniques from compressive sensing to aid PAPR reduction. This gave a much lower complexity algorithm based on linear programming instead of semi-positive definite relaxation. The new algorithm can be applied to full-frame transmissions in OFDM with as many as 128 subcarriers. In the OFDMA case, for users with small allocations, we can operate on frames as large as 1024 subcarriers. Preliminary results in this area were presented at the Information Theory and Application Workshop in February 2011, and will be submitted to an IEEE journal by the end of the 2010-2011 academic year.

Our investigations into implementing this PAPR algorithm on the software-defined GNU operating system radio platform were frustrated by GNU Radio's poorly developed software environment. Some test systems were implemented on the platform, but their performance saturated at very low rate, and we feel that the software customization promises of GNU Radio will be very hard to achieve for any algorithms with nontrivial complexity.

Pre-coding techniques for MIMO-OFDM were also briefly investigated. Our research was in the context of LTE coordinated multipoint (CoMP) transmissions.

Significance:
This work in power-efficient wireless communication builds knowledge in this area that may be applied to more-efficient military field communications, surveillance activities for nuclear weapons, and for infrastructure communication for homeland security applications.

Metrology of 3D Nanostructures
142440

Year 2 of 3
Principal Investigator: R. Boye

Project Purpose:
The goal of this project is to develop techniques for the inspection of 3D nanostructures. Such structures are critical for novel nanomanufacturing with potential applications including metamaterials, volume optics, nanoelectromechanical systems, photonic crystals, optical circuits, and other devices that control light propagation at the micro and nanoscale. However, better metrology methods are necessary to properly characterize and inspect these devices, particularly as these structures expand in volume and shrink in feature size. The feature sizes that can be fabricated are already several times smaller than the wavelength of visible light and, therefore, are beyond the resolution limit of a standard microscope (scanning electron microscopes can be used to form high-resolution images, but are limited in terms of sample preparation, speed, and cost).

Attempts to achieve super-resolution images beyond the half-wavelength limit should take advantage of all the information available. Prior knowledge of the sample can be used to increase the accuracy of the measurement. Super-resolution microscopy is experiencing a revolution as new approaches are applied to biological samples. In a process called PALM (photoactivated localization microscopy), sparse arrays of fluorescent molecules are sequentially photoactivated within a sample in a wide field of view. When light from a single fluorophore is collected, knowledge of the system's Point Spread Function (PSF) enables super-resolution down to about 20 nm1. A related technique, called STORM (stochastic optical reconstruction microscopy), uses a different type of emitter that enables controlled photoswitching to achieve similar resolution. More recently, attempts to achieve optical sectioning, and thus depth resolution in a wide-field technique, use spatiotemporal focusing of short pulses in combination with two-photon excitation fluorescence. This work is in collaboration with the University of Colorado at Boulder.

Summary of Accomplishments:
Work on this project made progress in the following areas.

- Temporal data from individual quantum dots was collected. Quantum dots blink in a characteristic fashion and the recorded temporal data can be used as a priori information to increase the resolution of microscopic imaging systems.

- Detailed simulations of super-resolution optical fluorescence imaging and independent component analysis were completed. These two techniques have been proven to provide substantial resolution enhancement for optical microscopy techniques.

Significance:
This project will advance the DOE’s goal of improving nanophotonics technology by improving 3D inspection techniques. Sandia’s expertise in creating large nanostructured samples requires matching techniques for inspection and metrology in 3D. Moreover, optical imaging with 3D super-resolution well beyond the wavelength of light has applications in medicine, biology, materials science, and nanofabrication inspection in both research and industrial settings.

Genetic Engineering of Cyanobacteria as Biodiesel Feedstock
142441

Year 2 of 4
Principal Investigator: A. Ruffing

Project Purpose:
The purpose of the project is to genetically engineer cyanobacteria for the production of hydrocarbons to be used for biodiesel feedstock. While most efforts in biofuel production from photosynthetic microorganisms focus on the natural oil-producing eukaryotic algae, this project investigates the use of fast-growing, prokaryotic photosynthetic organisms with established methods of genetic engineering. Moreover, cyanobacteria have been shown to naturally secrete hydrocarbons such as free fatty acids, simplifying the downstream collection and purification of the biodiesel feedstock. This is advantageous compared to the intracellular accumulation of triacylglyceride (lipid) in eukaryotic algae, which is difficult to extract.

A well-studied cyanobacterium, *Synechococcus elongatus* PCC 7942, is being engineered for the production of free-fatty acids (FFA), a potential biodiesel feedstock. For FFA production, the engineering strategy includes four main steps: 1) elimination of FFA metabolism, 2) removal of feedback inhibition of the fatty acid (FA) biosynthesis pathway, 3) improving carbon flux through the FA biosynthesis pathway, and 4) enhancing carbon fixation. The engineering strategy utilizes novel genes cloned from the green alga, *Chlamydomonas reinhardtii*. Because *C. reinhardtii* is a natural oil producer, the FA biosynthesis enzymes from this organism may have greater activity than the native enzymes. Genetic engineering of the natural fatty acid pathway may lead to changes in the cell and photosynthetic membranes. Several techniques are used to characterize changes in membrane composition and photosynthesis, including electrospray ionization-mass spectroscopy (ESI-MS), confocal hyperspectral fluorescence imaging, and pulse-amplitude-modulated (PAM) photosynthesis yield analysis. Changes at the genetic level are analyzed using ribonucleic (RNA)-seq, a sequence-based technology for analysis of gene expression levels. The principal investigator is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments:
The main scientific and technical accomplishments of this project are outlined based on project objectives:

Engineered *Synechococcus elongatus* produced FFA:
- FFA metabolism was eliminated through gene knockout of acyl acyl-carrier-protein (ACP) synthetase in *S. elongatus*.
- Expression of a truncated thioesterase from *Escherichia coli* increased FFA production in engineered *S. elongatus* by removing feedback inhibition of the FA biosynthesis pathway.
- Engineered *S. elongatus* produced over 50 mg/L of FFA.

Physiological changes in engineered *S. elongatus* were characterized:
- FFA-producing *S. elongatus* showed up to 60% reduction in final cell concentration. This has a significant impact on productivity, particularly for large-scale production.
- The decrease in cell concentration correlates with decreased photosynthetic yield and lower rates of oxygen evolution.
- FFA production also led to degradation of Chlorophyll-a and structural changes of the thylakoid membranes, as indicated by pigment aggregation at the cell poles.

Possible underlying mechanisms for these physiological changes were identified:

- Unsaturated FA, such as linolenic acid, was shown to be toxic to *S. elongatus*, inhibiting cell growth and leading to degradation of both phycobiliprotein and Chlorophyll-a pigments. This is likely due to oxidation of the unsaturated FA and production of reactive oxygen species.
- Electrospray ionization-mass spectrometry analysis of engineered *S. elongatus* shows changes in the chemical composition of FA in the thylakoid and cell membranes. These chemical changes may compromise the structural integrity of the membranes.

FA biosynthesis genes from *Chlamydomonas reinhardtii* were cloned and expressed in *S. elongates*: An acyl-ACP thioesterase from *C. reinhardtii* was expressed in *S. elongatus*, leading to a 40% increase in FFA production.

Significance:

The initial R&D accomplishments of this project demonstrate that cyanobacteria can be genetically engineered for hydrocarbon production. While it remains to be seen if the engineered cyanobacteria can produce hydrocarbon at the high levels required to support biofuel production, the construction of FFA-producing cyanobacteria illustrates the potential for biofuel production. This introduces a new photosynthetic candidate for hydrocarbon production, one that was previously overlooked due to its low level of natural lipids. With genetic modification, cyanobacteria can compete with the natural oil-producing algae which are the focus of most biodiesel research efforts in the scientific community. This project also contributes to the fundamental understanding of the physiological changes that accompany hydrocarbon production, an issue previously overlooked by the scientific community. The results of this project not only show that FFA production has negative physiological effects, they also indicate two possible mechanisms for these effects: the oxidation of unsaturated FA and changes in the chemical structure of membrane FA. The accomplishments of this project contribute to Sandia's Energy and Infrastructure Assurance mission and two themes of the DOE's strategic plan: Theme 1 Energy Security and Theme 3 Scientific Discovery and Innovation.

This project provides a foundation for the advancement of biofuel production using genetically engineered cyanobacteria. The engineered strains developed in this project may be further modified to optimize the potential for large-scale biofuel production. The novel genes cloned from *Chlamydomonas reinhardtii* may be used to enhance hydrocarbon production in other photosynthetic microorganisms, including other cyanobacterial strains and eukaryotic algae. Furthermore, the genetic engineering strategy employed in this project may be applied to improve hydrocarbon production in other microorganisms. In addition to advancing the development of hydrocarbon-producing strains, this project may also be leveraged to support the investigation of downstream processing including separation techniques, conversion to fuel, and analysis of fuel properties. The strains developed in this project, having the capability to produce and secrete FFA, may be leveraged to develop new technology for the separation and purification of FFA from the liquid culture. This project may also be leveraged to support the investigation of new techniques for converting the cyanobacterial FFAs into hydrocarbons with better fuel properties. Lastly, the combustion properties of the fuels developed from the cyanobacterial FFAs must be characterized.

Refereed Communications:

A.M. Ruffing, "Engineered Cyanobacteria: Teaching an Old Bug New Tricks," *Bioengineered Bugs*, vol. 2, p. N/A - open source, May 2011.

Enabling Self-Powered Ferroelectric Nanosensors: Fundamental Science of Interfacial Effects under Extreme Conditions
142543

Year 2 of 3
Principal Investigator: J. Ihlefeld

Project Purpose:
Physically small and unobtrusive devices that can sense and report on their environment without relying on limited lifetime external power sources (batteries) would be of tremendous use to both US industry and DOE defense missions. Ferroelectrics are ideal candidate materials for such compact sensors because their unique and coupled electrophysical properties mean that they could potentially draw power (via piezoelectric energy harvesting, for example) from the very environments that they are sensing. Recent advances in fabrication have made possible the thought of economical nanosensors based on ferroelectrics.

The purpose of this project is to study the effects of extreme environments on the performance of these materials. We have assembled a cohesive team of diverse experts to evaluate the fundamental limitations of operating such potentially self-powering sensors in extreme application-relevant (e.g., corrosive, radiation rich, high-temperature) environments. We will evaluate intrinsic effects of such environments on the integrity and electrical performance of nanoscale ferroelectrics as well as changes in response related to the ferroelectric-electrode interface, both of which are critical to determining the feasibility of developing and deploying the envisioned self-powered sensors. This project entails collaborations with the University of Florida, the University of Texas-Austin, and Rensselaer Polytechnic Institute.

Summary of Accomplishments:
All project milestones for FY 2010 and FY 2011 have been met, including the following:
1. We fabricated initial structures, distributed to partner institutions, and completely physically and electrically characterized materials
2. We performed initial bulk material corrosion studies
3. We performed nanoscale phase evolution vs. temperature studies at national light source
4. We characterized in situ lead zirconate titanate (PZT) film in a corrosive environment
5. We characterization structures submitted to radiation environments.

Additional noteworthy accomplishments include:
1. We developed an automated scanning electrochemical cell for use in this project that enables highly versatile electrochemical characterization.
2. We developed a new electrode technology that results in chemically homogeneous PZT films with previously unachieved ferroelectric and piezoelectric performance. We prepared a chemically homogeneous PZT film prepared from a single chemical solution that marks a tremendous technological breakthrough that will have broad impacts outside of this project. A Sandia invention disclosure has been filed on this technology. This project has resulted in 5 invited talks at university seminars and international conferences and 18 contributed presentations at international conferences and workshops. One manuscript has been published in a peer-reviewed journal and one additional manuscript has been submitted.

The project goals of fabrication of electrode-ferroelectric composites and quantitative analysis of initial structures in extreme environments have been met. To meet these goals and milestones, we have facilitated the interaction of the three university teams to study the effects of corrosion and radiation on the microstructural and ferroelectric performance of the ferroelectric films prepared at Sandia.

Significance:
The scientific understanding developed by Sandia and our university partners will substantially impact DOE, DHS, DoD, and other agencies interested in the future development of unobtrusive self-powering sensors. For example, knowing exactly how these nanoscale systems respond in a variety of radiation environments will assist with the evaluation of materials for satellite systems, as well as for potential unattended sensors to monitor the transport of illicit radioactive material. Further, stability of such nanoscale materials systems in corrosive chemical environments, particularly those relevant to marine and/or petrochemical applications, will be of interest to DoD as well as to US industry.

Our ability to prepare the best possible material will greatly impact the general scientific community by allowing us to probe true fundamental material and system properties devoid of extrinsic issues related to material defects. This will maintain Sandia's leadership in the area of ferroelectric thin film research.

Refereed Communications:
J. Graham, S. Landsberger, P.J. Ferreira, J. Ihlefeld, and G. Brennecka, "Neutron Flux Characterization Techniques for Radiation Effects Studies," *Journal of Radioanalytical and Nuclear Chemistry*, pp. 1-5, June 2011.

Integration of Block-Copolymer with Nanoimprint Lithography: Pushing the Boundaries of Emerging Nanopatterning Technology
145832

Year 2 of 3
Principal Investigator: G. L. Brennecka

Project Purpose:
The rapid pace of innovation enabling Moore's Law (doubling transistor density every ~1.5 years) is of great importance to our nation's technological leadership and economic security. To maintain this pace, the International Technology Roadmap for Semiconductors (ITRS) prescribes an 11-nm half-pitch for dense patterns and 4.5-nm critical dimensions by 2022. Current 193-nm immersion optical lithography can print ~40-nm half-pitch and may reach 20 nm with double patterning. Extreme ultra-violet (EUV) lithography persistently raises doubts due to the costly complete change of infrastructure. Therefore, alternative lithographic pathways to the extreme nanoscale ITRS goals are needed. We propose to direct the self-assembly of block copolymers (BCP) into device-oriented patterns fabricated by optical interferometric lithography (IL), use those self-assembled BCP patterns as masks to create nanoimprint lithography (NIL) masters via plasma etching, and fabricate prototype devices using this combined top-down and bottom-up approach.

BCP-based patterning techniques excel at extreme nanoscale feature definition but have significant limitations related to defect density, long range order, and the fabrication of multiple feature types on a single wafer. Using IL-directed BCP, we will achieve long range order across device-relevant dimensions, and by building up a single NIL master from multiple IL+BCP directed self-assembly (DSA) coupons, we will be able to fabricate essentially arbitrary patterns of extreme nanofeatures unencumbered by optical diffraction limitations. Extensive metrology associated with relevant characteristics (critical dimensions, line edge roughness, pattern fidelity, defect density and distribution, etc.) at every stage of the process will provide guidance about the eventual feasibility of this approach. This project is the first combination of IL with BCP and NIL technologies, and will define the limits of a combined top-down/bottom-up lithography approach for use in commercial applications including integrated circuit manufacture.

Summary of Accomplishments:
The University of New Mexico interferometric lithography (IL) process (and associated antireflection coatings) has been extended to multiple substrates of interest, including Si/SiO_2, Si_3N_4-coated Si, BK7 glass, and fused silica. These IL patterns have directed the self-assembly of University of Washington (UW) block copolymer (BCP) features, with reliable 3x feature density multiplication and demonstration of 4x density multiplication. Use of a photopatternable cross-linked mat to define the chemical pattern, in conjunction with an end-grafted polymer brush greatly assists in the resolution and reliability of the DSA process.

Etch processes have been developed in facilities at UW and Sandia for the transfer of BCP-defined patterns with ~20-nm features into underlying substrate layers, and such masters have been used as templates for NIL master fabrication and subsequent patterning. Modeling and simulation efforts associated with how the substrate-BCP interface alters the thermodynamic stability of the BCP thin film system relative to the bulk continue with great success. These efforts have reached sufficient fidelity to begin to provide relevant information about the kinetics of the assembly processes.

So far, this project has resulted in 26 presentations (11 of them invited) and 4 peer-reviewed publications, one featured on the cover of *Macromolecules*.

Significance:
Extending nanopatterning capabilities at Sandia will fill a current gap and enhance/enable many critical missions involving materials, nanoscience, nanodevices, and device-system integration. Specific applications include plasmonic, photonic, and phononic devices for use in controlling electro-optical interactions within materials, high-sensitivity chem-bio sensors, future complementary metal oxide semiconductor (CMOS)-based electronics, nanoelectromechanical systems (NEMS), and renewable energy harvesting and storage. Because of the broad implications of this work and the staggering array of devices that it could enable/improve, the potential technical impacts literally span all agencies; however, DHS, DoD, and others that have a stake in Sandia-manufactured nanoscale electronic/photonic devices should be particularly interested.

Refereed Communications:
C.Y.P. Yang, E.L. Yang, C.A. Steinhaus, C.-C. Liu, P.F. Nealey, and J.L. Skinner, "Planar-Localized Surface Plasmon Resonance Device by Block-Copolymer and Nanoimprint Lithography Fabrication Methods," to be published in the *Journal of Vacuum Science and Technology B*.

Performance Monitoring and Enhancement in Data Center
145970

Year 2 of 2
Principal Investigator: Y. R. Choe

Project Purpose:
With the growth of data and need to process them, data center (DC) or large computing clusters have become an important computational paradigm to deal with this data explosion. Whether offered as an open cloud service or running proprietary solutions, the services offered by data center are an important selling point for data center owners. Here, we are concerned with services offered that can enhance the performance and ability of users utilizing such data center resources.

One way to enhance data centers' performance is to ensure they can react to faults. Fault scenarios can be complicated, however. Other than hardware failures, services within a data center can fail without notice due to software bugs or network conditions (e.g., high congestion). The ability to monitor DC environment, at the hardware and service level, and to react to anomalous behaviors is essential to ensure that DC remains a high-value asset. It is also important that DC operators and users are aware of failures, and can react to failures independently to ensure that their operations can continue or degrade gracefully. It is then important to offer monitoring, detection, and recovery of failures as services to both network operators and users. The work is in collaboration with the University of California at Davis.

Another vector to enhance performance is to allow network components to be offered as an "open platform." By open platform we mean that users can easily and expressively indicate the requirement for their services, and the network can automatically adjust the service (by moving them within the DC, for example) to satisfy the requirement. The issue here is the implementation of a service in the network that would allow such a dynamic change to users' services. Offering network as a service, beyond the traditional packet delivery, is an important value-added feature that could benefit network operators and users.

Summary of Accomplishments:
For a study of measurement tool's impact, we performed experimental evaluations of the performance impact that packet-capturing process have on web (HTTP) servers. We found that packet-capturing processes impact the performance of web servers, but the impact varies depending on whether or not the packet capturing and web processes are collocated on the same CPU core. We found that collocating the capturing and web server process degrades the performance of web servers severely, unless the application server forks many processes to monopolize the resource scheduling. We also noted statistically significant performance degradation even when the two processes are not collocated, suggesting there is another source of contention that causes performance degradation.

For modeling the measurement problem, we proposed a simple matching game between two players, as a gadget for us to understand the complexity of end-to-end passive measurement with resource constraint. In this game, we assumed two players, each with a limited amount of resource in each time slot, and each able to spend the resource on inspecting the network events from the same application occurring during each time slot. Assuming one player's sampling strategy is known, the goal of the game is for the second player to optimize his/her strategy so the total number of matched events (events sampled by both players) over N time slots is maximized. The optimal strategy for this problem, as we understand now, is factorial expression, and we are in the process of determining whether a closed-form solution exists. In addition, the formulation for this problem becomes more complicated as the number of players increases (i.e., longer end-to-end path) and as there are more types of network event to monitor (i.e., more application streams to monitor).

Significance:
With the explosive growth in computing power and storage capacity, data center management has become more difficult. With this work, identifying the bottlenecks and designing automated methods to enhance them are being explored. This work can benefit the cloud computing community, and the efforts of DOE and other federal partners in exploring cloud concepts. DHS is also consolidating data centers to consider a private cloud.

Advanced Constitutive Models for Thermally Activated Shape Memory Polymers: Connecting Structure to Function
146013

Year 2 of 3
Principal Investigator: J. A. Zimmerman

Project Purpose:
Thermally activated shape memory polymers (SMP) can be manufactured to memorize a permanent shape, programmed thermomechanically to hold a temporary shape, then deployed back to its permanent shape in response to a specific temperature event. Compared to shape memory alloys, SMPs are inexpensive to manufacture. They are malleable and damage tolerant, and can undergo large, controllable shape changes in excess of 100% strain. SMPs are being investigated for a variety of applications, including temperature sensors, deployable and morphing structures for aerospace and biomedical. The shape memory performance depends on the complex interactions of many microstructural and thermomechanical factors, and considerable opportunities exist to tailor the polymer structure and the thermomechanical programming procedure to achieve the desired shape memory performance.

Research conducted by Presidential Early Career Award for Scientists and Engineers (PECASE) winner, Professor Thao D. Nguyen, at Johns Hopkins University initially focused on type I SMPs described by covalently cross-linked amorphous networks. The shape memory effect is provided by the equilibrium configuration of the cross-linked network. Shape storage and recovery is achieved by the glass transition and is strongly influenced by viscoelastic relaxation. While the thermomechanical properties of SMPs are highly customizable, the connections between thermomechanical properties and shape memory performance are unclear. Our goal is to develop advanced constitutive models for SMPs to study the connection between polymer structure, thermomechanical properties, and shape memory performance.

Summary of Accomplishments:
We developed a thermoviscoelastic model for amorphous networks that incorporated the effects of a broad stress and structural relaxation spectrum above the glass transition temperature T_g and yielding and post-yield softening below T_g. Structural relaxation was modeled by P serial time-dependent processes, each described by a temperature- and structure-dependent flow rule for the partial nonequilibrium volume change. Viscoelastic relaxation was modeled using N parallel time-dependent processes, each described by a flow rule for the partial nonequilibrium stress dependent on the temperature, structure, and flow stress. Yielding was characterized by a single yield strength, which evolved with the effective plastic strain rate to produce the post-yield softening response.

Parameters of the stress relaxation processes were determined from time-temperature superposition tests, which measured the master curve of the frequency dependence of the storage modulus. To characterize the structural relaxation processes, we developed an isothermal recovery test to measure the master curve of the time-dependent recovery response to a step change in temperature. We also developed isothermal compression tests to characterize the rate-dependence of the yield strength. Results of an isothermal compression test for tBA-co-PEGDMA (tert-butyl acrylate (poly(ethylene-glycol)n dimethacrylate) with 10 wt% crosslink density show excellent agreement between experiments and simulations for the strain-rate dependence and temperature-dependence of the stress response through the glass transition.

The model was applied to predict the partially constrained recovery response of the tBA-co-PEGDMA network as observed by experiments. Cylindrical specimens were deformed below T_g to program a temporary shape. The specimens were heated to above the T_g under a constant constraining stress to recover partially the programmed deformation. Our model was able to predict important features of the measured response, including the overshoot in the recovered strain at temperatures near the T_g. We are currently preparing a manuscript for the thermoviscoelastic model and its application to model partially constrained recovery.

Significance:
This project provides state-of-the-art predictive capability for Sandia in the modeling and simulation of polymers. This capability is needed to accurately assess the thermomechanical response of such materials and their suitability within Sandia's technology products. The modeling studies provide a fundamental understanding between the thermoviscoelastic properties and thermomechanical loading conditions, and the recovery behavior of shape memory polymers, which is needed for the developmental of computational tools for the efficient design and optimization of SMP materials and devices. Moreover, the modeling studies advance the development of a continuum-modeling framework for finite deformation thermoviscoelasticity.

This work supports the mission of the DOE through scientific discovery and innovation in physical science, engineering, and emerging scientific disciplines by developing advanced models for the physical response of polymers and polymer composites. When coupled with models for piezoelectric materials, this effort presents unique possibilities for the design and development of non-powered, self-aware sensors suitable for DOE, DoD and DHS applications.

Scalable Assembly of Patterned Ordered Functional Micelle Arrays
146152

Year 2 of 3
Principal Investigator: H. Fan

Project Purpose:
Successful multiscale patterning (micro- to nanometer) with precision, speed, and reproducibility at the nanoscale is crucial for rapid evolution in computer logic, memory, metamaterials, photonic crystals, plasmonics, energy harvesting and storage, and nano-bio applications. Significant advances in nanopatterning technology combine "bottom-up" directed self-assembly with "top-down" lithographies, producing sub-100-nm features. However, control of nanoscale structures in the third dimension remains an unsolved challenge. Significant technical difficulties include scalable, cost-effective, and rapid fabrication of reliable patterns with low defect densities and long-range order in various materials systems. We are studying self-assembly of amphiphilic molecular micelles to form large-area arrays on patterned surfaces, and in 3D nanoscale templates with an emphasis on compatibility with semiconductor processing for future device integration. Amphiphilic molecules form monodisperse micelles with sizes precisely defined by molecular chain length of each amphiphilic molecule, ranging from 5-50 nm. Evaporation of micellar solutions leads to highly ordered large-area micelle arrays.

Dynamic micelle assembly, operating under the influence of physical 1D-3D topographical templates with characteristic dimensions integer multiples of one to five times the micelle diameter, will provide a means to spatially control long-range order and to direct micelle assembly into predefined hierarchical configurations. Through encapsulation, various metal, semiconductor, or magnetic nanoparticles can be introduced into the hydrophobic interior, providing unprecedented engineering of robust hybrid functional 1D-3D micelle arrays and their collective electronic, optical, or magnetic behaviors. For example, although the behavior of periodic dielectric structures, so-called "photonic crystals," are quite well understood, the response of metallo-dielectric structures with coupled collective plasmonic and dielectric responses are quite poorly understood, despite their great potential application in advanced devices. Precise nanoscale patterning of these arrays will enable fabrication of controlled nanostructures for devices such as surface enhanced Raman sensors and photonic crystals.

Summary of Accomplishments:

- Developed a micro-injection process to synthesize water-soluble monodisperse polymer nanoparticles with narrow size distributions. We used amphiphilic polystyrene-b-polyvinylpyridine (PS-PVP), as a main structure-directing agent. Gradual injection of acidic aqueous solution protonates PVP blocks to become water soluble, which induces self-assembly of PS-PVP to form hydrophilic nanoparticles. Through control of injection speed and size of segments of PS and/or PVP, we were able to control phase transition of PS-PVP, which consequently allows tuning nanoparticle size and size distribution. These nanoparticles formed long-range ordered 2D and 3D arrays revealed by both scanning electron microscopy (SEM) and ultraviolet-visible (UV-vis) spectroscopy. The polymer chains expand by electrostatic forces or electrostatic repulsion, depending on the extent of protonation. We showed that the nanoparticle size is pH-sensitive due to the charge interactions within positively charged PVP chains during protonation/deprotonation.
- Assembled monodisperse polymeric micelles into topographically patterned substrates with high precision. Using chemically derivatized, topographically complex, substrates amphiphilic PS-PVP micelles were assembled by dip coating into each topographic feature. The number of micelles per feature followed the expected "magic number" which maximized packing of the micelles in the feature. The number of micelles per feature was best fit to the 250-nm diameter, indicating that during assembly, the micelles are partially dehydrated. Micelles were assembled into features

ranging from 200 nm–1µm in diameter. The templates for directed self-assembly specifically consisted of arrays of cylindrical recessed features selectively functionalized with charged molecular monolayers (either attractive or repulsive to PVP, depending on the specific experiment).

- 3D template fabrication. We have now fabricated through interference holography 3D chemically derivatized substrates with characteristic dimensions on the same scale as the PS-PVP micelles. Additionally, imprinting lithography has also been demonstrated for 3D patterns.

Significance:
This work provides bottom-up methods for the synthesis and control of matter on multiple length scales. The new nanostructures and the degree of control would provide benefits to energy and national security applications. Fabrication of scalable patterned structures and facile and scalable self-assembly processes for ordered arrays, and their use as templates for metallic nanostructures in energy storage, photonic, and sensor applications, will impact DOE and DHS missions in national security.

Refereed Communications:
K.A. Arpin, J.H. Pikul, W.P. King, H. Fan and P.V. Braun, "Template Directed Assembly of Dynamic Micellar Nanoparticles," *Soft Matter*, vol. 7, pp. 10252-10257, September 2011.

Descriptions and Comparisons of Brain Microvasculature via Random Graph Models
151368

Year 1 of 2
Principal Investigator: R. Schiek

Project Purpose:
Brain tissue includes a close interaction of neurons, glial cells, and microvasculature. This project, in collaboration with Cornell University, will increase knowledge of the microvasculature by extracting maps of the microvasculature from two-photon optical 3D imagery, describing such maps as random graphs, and developing statistical tools for comparing the graphs.

The project will use microscopy methods developed at Cornell University for the study of micro-strokes, which are designed to highlight the vascular system of the brain cortex of live mice. The resolution is approximately one micron laterally and somewhat less in depth to a maximum depth of 0.5 to 1 millimeter which, for mouse cortex, is nearly full thickness. The project plan includes three activities:

1. Develop computational methods to extract complete maps of the cortex microvasculature from the 3D images based on angiographic medical imaging techniques.
2. Develop methods for computing generative random-graph models of the map based on estimating the probability laws (or the parameter in the probability laws) that generate the random graphs. This requires estimation algorithms for space-dependent graph structures since the cortex changes with depth below the surface (i.e., cortical levels) and is organized laterally in columns. Furthermore, the map of will have errors (both true edges missing and false edges inserted) so a model for errors (possibly with unknown parameters to be estimated) is required. Finally, edges are marked with the physical length and diameter of the corresponding vessel and generative models for these marks, possibly correlated with the graph itself, are desirable.
3. Develop statistical tests for comparing graphs in order to determine whether a particular chronic intervention leads to a change in the microvasculature. The interventions could be therapeutic (e.g., a drug or neurostimulator) or environmental (e.g., chronic stress).

Summary of Accomplishments:
Collaborators at Weill Cornell Medical College) and Sungkyunkwan University, Korea, have developed an experimental apparatus and protocol for recording optical video reflectance spectroscopy data at 570 nm and 610 nm for the study of the neurovascular system in epilepsy and other brain disorders both peri-operatively in human patients and in rodents. The basic output is video (10 frames/second, 768 x 480 pixels/frame, 11.7 x 14.6 microns/pixel) of the optical reflectance at 570 nm and 610 nm from which the amount of oxygenated and deoxygenated hemoglobin in each pixel can be calculated. Therefore, these invasive measurements in 2D are higher spatial- and temporal-resolution analogs of the noninvasive measurements made in 3D in the in-functional magnetic resonance image (fMRI). To quantitatively describe the temporal and spatial connections between the electrical and vascular activity of the cortex, a multilayer layer electrical circuit model has been developed. The model, efforts to identify the parameters in the model from the optical data, and use of the model in video processing have occurred.

Significance:
Ties to the DOE mission of the proposed project include the following:

- In neuroscience (pure and applied), the work will provide a quantitative description of the microvasculature and methods to determine whether it is affected by interventions. Interventions include chronic therapies (e.g., drugs, neural stimulators), chronic environmental characteristics (e.g., stress), and chronic sequelae of acute events (e.g., traumatic brain injury).
- In random graph methodology relevant to defense intelligence missions, the work will provide statistical methods to estimate graph models when the data is corrupted and the graph is known to have structure such as limits on vertex degree.

Refereed Communications:
T.P. Santisakultarm, N.R. Cornelius, N. Nishimura, A.I. Schaffer, R.T. Silver, P.C. Doerschuk, W.L. Olbricht, and C.B. Schaffer, "In Vivo Two-Photon Excited Fluorescence Microscopy Reveals Cardiac- and Respiration-Dependent Pulsatile Blood Flow in Cortical Blood Vessels in Mice," to be published in the *American Journal of Physiology*.

J. Sunwoo, N.R. Cornelius, P.C. Doerschuk, and C.B. Schaffer, "Estimating Brain Microvascular Blood Flows from Partial Two-Photon Microscopy Data by Computation with a Circuit Model," in proceedings of the 33rd Annual International Conference of the *IEEE EMBS*, August 2011.

Development of Novel Nanoarchitectures to Enhance High-Temperature Thermoelectric Oxides for Clean Energy Harvesting
151369

Year 1 of 3
Principal Investigator: N. S. Bell

Project Purpose:
The purpose of this project is to develop novel thermoelectric material structures for the capture of energy from waste heat sources from existing systems. Materials processing to create porous thermoelectric materials will lower the thermal conduction of the active oxide while allowing for electrical conduction, and thereby raise the figure of merit for the existing oxide. The technique for generating the porous ceramics focuses on the creation of nonwoven fiber mats using electrospinning of polymer solutions containing sol-gel precursors. These nonwoven mats are converted to porous ceramics by mechanical pressing and thermal conversion, leading to bulk wafers with interconnected networks of air (for thermal barrier behavior) and the ceramic, in this case Nb-doped TiO_2 (anatase). Nb doping raises the conductivity of the titania (TiO_2) network, while maintaining thermal stability. Processing conditions also affect surface roughness of the materials, leading to lower surface conductivity, and the formation of nanosized grains, again benefiting low thermal conductivity. By understanding processing controls, the performance of a bulk material can be improved and lead to new opportunities for energy capture and energy efficiency at relatively low cost.

Summary of Accomplishments:
In this project, electrospinning was successful in fabricating porous, fibrous networks of Nb-doped TiO_2, both as random and as oriented networks. Pressing of the initial fibers generated a ribbon like morphology. Grain sizes are extremely small, on the order of 7 nm by line broadening characterization from x-ray peak broadening (Scherrer Equation). Doping of the TiO_2 remains single phase up to contents as high as 20 mole percent Niobium. High-temperature sintering up to temperatures of 1000 °C increases grain size to approximately 41 nm, within fibers with diameters of ~100 nm.

Initial pressing under high pressure leads to ribbon-like materials, and extremely fragile samples after calcination at 500 °C or higher. Using lower pressing pressure and longer hold times allows for consolidation and rearrangement of the fibers to form a more resilient network. Nanotubes were also formed, which increases phonon scattering and increases the rate at which fibers can be made with small dimensions. These can be used to form the ideal nanoribbons upon pressing, giving extreme anisotropy between the structures. The thickness of the nanoribbons are ~50 nm with width of near 2,500 nm. Measurements of thermoelectric properties were attempted by Dr. Han Ill-You (Seoul University). He reported that electrical contacts were difficult to form, and that the samples were mechanically very fragile. They also found that the TiO_2-Nb (2%) would not be reduced under hydrogen atmosphere calcination to give electrically conductive samples. This is highly unexpected, and ongoing study into the method for reduction is being pursued.

Significance:
This work will benefit applications in power collection from thermal sources and, therefore, can be applied to a broad spectrum of operations related to waste heat generation in both stationary power technologies and in transportation. These technologies will benefit the DOE and national security with respect to energy generation and energy efficiency and can be envisioned to apply to remote power needs, operations in extreme environments, or device efficiency.

Reconstruction of a High-Resolution Late Holocene Arctic Paleoclimate Record from Colville River Delta Sediments
151370

Year 1 of 3
Principal Investigator: T. S. Lowry

Project Purpose:
The purpose of this project is to differentiate between the effects of long-term climate change and the Arctic Oscillation on changing terrestrial vegetation in the Arctic. Current climatic predictions of anthropogenic global warming indicate that Arctic regions will become warmer and wetter by 2100, and that temperature increases in the northern high latitudes could be as much as 3 to 7 °C. The instrumental record in the Arctic goes back only a few decades and a paucity of knowledge, therefore, exists concerning recent and Holocene climate change in the Arctic. It is difficult to determine whether year-to-year weather changes occur due to long-term trends and, in turn, whether those trends are related to changes in atmospheric circulation mechanisms such as the Arctic Oscillation. Sediment cores from the Colville River delta and Simpson's Lagoon in the Beaufort Sea will be used to: 1) determine historical changes, and make predictions about future changes, in the sources and amounts of organic carbon input to the delta, and 2) reconstruct the changes in terrestrial vegetation of the watershed over the recent Holocene.

Summary of Accomplishments:
This study explores carbon input from the Colville River into its delta and the adjacent Simpson's Lagoon over the past 1000 to 2000 years, using core material and land samples taken during a 2010 field campaign. The Colville is the largest North American river that drains only continuously permafrosted soils, originating in the Brooks Range and flowing over the Alaskan North Slope into the Beaufort Sea. Preliminary x-radiographic analysis of these cores indicates they are well laminated, with minor bioturbation and no ice-gouging disturbance. Stable carbon isotopic analysis combined with lignin-phenol and algal pigment biomarkers are used to trace the inputs of organic carbon into these sediments throughout the late Holocene and indicate that terrestrial runoff has changed significantly over the time period represented in the cores, likely from increasing river flow, woody plant encroachment onto the tundra, and increasing expanse of permafrost lakes, all of which are documented phenomena in the Arctic.

Significance:
This effort will benefit DOE's Climate and Environmental Sciences Divisions' mission to "improve the scientific basis for assessing potential consequences of climate changes" by providing "the data that will enable an objective assessment of the potential for, and consequences of, global warming." The main objective of this project, which is to determine how terrestrial vegetation has changed in response to climate change and atmospheric oscillations over the past 2,000 years on the continuous permafrost of the north slope of Alaska, is directly aligned with the goals of the Office of Science Division of Biological and Environmental Research.

Experimental Bed Load Transport in Meandering Channels
151371

Year 1 of 1
Principal Investigator: V. C. Tidwell

Project Purpose:
River meander migration is one of the most perplexing and intriguing problems in open channel hydraulics. Significant progress in understanding this phenomenon has been accomplished only in the past few decades. While significant efforts toward understanding the relationships between sinuosity and sediment transport have led researchers to collect large datasets on natural rivers, relatively few laboratory experiments were conducted to date. The newly constructed sediment flume at the University of Arizona Civil Engineering and Engineering Mechanics Department offers a unique opportunity to shed insight into these relations.

Several researchers found that bedload transport is the dominant mechanism driving planform evolution. As erosion occurs at the toe of the outer bank, adhesive forces holding the bank are overcome by gravitation forces on the bank block. Hydraulic forces then carry this new source of bed load downstream. Hydraulic forces are believed to be greatest at the concave bank resulting in growth of meander bends. Due to the complexity of meander geometry, transverse and downstream bed slope, as well as stratification, cohesion, and vegetation along stream banks, the mechanics of sediment transport in meandering streams is difficult to simulate.

The most commonly applied meander evolution model employs the product of a linear coefficient and an estimate of the downstream velocity around a meander bend, based on the quasi-2D analytical solution to the Navier-Stokes Equation for incompressible and steady flow. This work couples laboratory and numerical experimentation to advance our understanding of this complex phenomenon and our ability to manage meandering rivers.

Summary of Accomplishments:
Project accomplishments are organized according to three key studies. The first study compared observed data for bank erosion and river meander to the first-order analytical solutions derived by two researchers. Because the migration of meandering channels consists of downstream translation, lateral expansion, and downstream or upstream rotations, several measures were formulated to determine which of the resulting platform is closest to the experimental data. Results from the deterministic model were found to be highly dependent on the calibrated erosion coefficient.

The second study focused on the dynamics of sediment plug formation. During high flows in the years 1991, 1995, 2005, and 2008, a sediment plug formed in the San Marcial reach of the Middle Rio Grande. The 2008 event was used to study the relationships between hydro and geomorphic variables that led to the development of the sediment plug. Three-dimensional hydrodynamic and sediment modeling was done using Delft3D and compared to US Geological Survey (USGS) flow gauge data at the Highway 380 and San Marcial Bridges, along with a flow loss function derived from gauge data. Results suggest the existence of thresholds for plug formation and that the contribution of specific variables to plug formation is not uniform.

The third study developed a guidebook toward river restoration with a particular focus on understanding river geomorphology and hydrologic process. The guidebook assists in identifying fundamental processes that shape a stream, how and why these processes have changed in the recent past, as well as how streams react during floods or high water. In the context of river restoration/rehabilitation, this information can be used to determine the scope, scale, and probability of success and sustainability of project design alternatives.

Significance:
This effort will directly benefits DOE's environmental technologies mission and is focused on improved understanding of water quality as impacted by river meander bank erosion. The safety, security, reliability and sustainability of environmental resources and human infrastructure must consider river management practices (e.g., reservoir releases) and their impact on bank erosion. In this project, tools and understanding are developed to inform public policy analysis to aid in identifying timely, cost-effective, and comprehensive resource management solutions. Linkages between reservoir operations, river flows, bank erosion and water quality are particularly important to thermoelectric and hydroelectric power production. In this way, efforts from this project will have direct application to DOE's hydropower mission, and infrastructure security mission.

Refereed Communications:
A.J. Posner and G. Duan, "Simulating River Meandering Processes using Stochastic Bank Erosion Coefficient," to be published in *Geomorpholog, Special Issue: Meandering Channels*.

Coupled Electrical, Electrochemical, and Thermal Performance of Large Format Lithium-Ion Batteries with Internal Cooling
151372

Year 1 of 1
Principal Investigator: C. Orendorff

Project Purpose:
Energy-storing electrochemical batteries are the most critical components of hybrid and electric vehicles (HEV and EV). Lithium-ion batteries are proposed to improve the fuel economy of these vehicles because of their higher specific energy, but face thermal management challenges. This research addresses the singular limiting feature of battery cooling systems — the cooling systems are external to the batteries, which implies that substantial temperature gradients exist between the heat generation location (the cells) and the skin of the battery. The internal cooling system approached in this project utilizes microchannels inserted into the interior of the cell that contain a liquid-vapor phase change fluid for heat removal at the source of heat generation. Although there have been prior investigations of phase change at the microscales, flow of pure refrigerants at the low mass fluxes experienced in the passive internal cooling system is not well understood.

In addition, existing thermal models for lithium-ion batteries have not adequately addressed the impact of thermal management on electrochemical performance. In this project, a fully coupled electrochemical and thermal model is developed for a flat spirally wound lithium-ion battery that can be readily used in HEV simulations to assess the impact of different thermal management strategies, including an experimentally validated internal cooling system.

Summary of Accomplishments:
Passive, thermally driven refrigerant (R134a) flow in a representative test section geometry (3.175 mm × 160 μm) was investigated using a surrogate heat source. Heat inputs were varied over a wide range of values representative of battery operating conditions (120 < < 6500 W L^{-1}). The measured mass flow rate and test section outlet quality from these experiments were utilized to accurately calculate the two-phase frictional pressure drop in the test section, which is the dominant loss mechanism in the passive system in most cases. Subsequently, a new correlation for buoyancy driven two-phase pressure drop was developed, which predicts the data more accurately than extending previous models beyond their range of applicability.

The two-phase frictional pressure drop model was used to predict the performance of a passive internal cooling system. This thermal-hydraulic performance model was coupled to the electrochemical-thermal model previously developed for performance assessment of two-scaled-up HEV battery packs (9.6 kWh based on 8 amp-hour [Ah] and 20 Ah cells) subjected to an aggressive highway dynamic simulation. Preliminary results show that internally cooled cells reduce peak temperature without imposing significant thermal gradients, especially when cycled more aggressively.

Significance:
This work represents the first-ever study of coupled electrochemical-thermal phenomena in batteries, from the electrochemical heat generation to the dynamic heat removal in actual HEV drive cycles. The proposed cooling system passively removes heat almost isothermally with negligible thermal resistances between the heat source and cooling fluid, thereby allowing battery performance to improve unimpeded by thermal limitations. By coupling the battery and internal cooling system models, this research demonstrates the pack size reduction achievable from improved thermal management. Preliminary results show that packs with internal cooling can be cycled more aggressively, leading to higher charge

and discharge energy extraction densities in spite of the volume increase due to 160 µm channels inserted into the 284.5 µm unit cell.

Refereed Communications:

T.M. Bandhauer, T.F. Fuller, and S. Garimella, "A Critical Review of Thermal Issues in Lithium-Ion Batteries," *Journal of the Electrochemical Society*, vol. 158 pp. R1-R25, January 2011.

T.M. Bandhauer, T.F. Fuller, and S. Garimella, "A Coupled Electrochemical, Thermal, and Current Collection Model for Spirally Wound Lithium-Ion Batteries," to be published in the *Journal of the Electrochemical Society*.

T.M. Bandhauer and S. Garimella, "Experimental Demonstration and Performance Validation of a High-Flux, Passive, Internal Thermal Management System using Microscale Liquid-Vapor Phase Change," to be published in *Applied Thermal Engineering*.

T.M. Bandhauer, T.F. Fuller, and S. Garimella, "A 2-D Coupled Electrochemical and Thermal Model for Spirally Wound Lithium-Ion Batteries," to be published in the *Journal of the Electrochemical Society*.

T.M. Bandhauer, T.F. Fuller, and S. Garimella, "Temperature Dependent Electrochemical Heat Generation in a Commercial Lithium-Ion Battery," to be published in the *Journal of Power Sources*.

Discriminative Feature-Rich Models for Syntax-Based Machine Translation
151373

Year 1 of 2
Principal Investigator: K. R. Dixon

Project Purpose:
In the past few years, automatic machine-translation (MT) systems have progressed significantly. These MT systems take text from a source language and attempt to generate text with the same meaning in a target language. While the performance of these systems is improving steadily, any user of MT systems knows that their performance still has a long way to go to reach the level of human translators.

For years, standard MT systems have assumed that the features of the language-translation problem are local to the words being decoded. While this assumption is obviously incorrect and virtually always violated in all languages of interest, MT systems assume feature locality to make the translation problem computationally and mathematically tractable. Recent advances using long-distance language features have created state-of-the-art performance gains for many tasks in natural language understanding, such as question answering and automatic summarization. However, these features have received scant attention from machine-translation researchers due to the mathematical complexity and computational burden of relaxing traditional local-feature assumptions.

In this project, we are seeking to improve the performance of MT systems by exploring theoretical and empirical effects of nonlocal features. Because this is a relatively new area of research, we will first create various nonlocal, cross-language features to address frequent errors made by MT systems. With these nonlocal features in hand, we will develop novel translation algorithms based on violating the long-held local-feature assumption. Finally, we will analyze and demonstrate the performance of creating translation models using machine-learning techniques that exploit the nonlocal features.

Summary of Accomplishments:

- Improved search algorithms for machine translation with nonlocal features:
  We have pursued the addition of syntactic translation rules that violate independence assumptions of standard search algorithms (hence making them "nonlocal") to further the goal of combining the advantages of multiple approaches to machine translation in a single model. This will build on our machine translation system (presented at a conference), which combined the most popular approach — "phrase-based machine translation" — with syntactic information from dependency syntax. The next step is to make the search algorithm more flexible so that it can incorporate larger syntactic translation rules from other syntactic formalisms (such as synchronous context-free grammar and synchronous tree-adjoining grammar).
- Models for discovery of large translation templates:
  We are exploiting Bayesian nonparametrics in defining a model to discover large, templatic constructions in "parallel" text (text paired with its translations from a human translator). Performing posterior inference with this model will let us discover bilingual templates, identify where slots are present within them, and perform clustering of words to define sets of interchangeable items to fill each type of slot. We plan to integrate these templates into the same system mentioned above as additional nonlocal features.

Significance:
This project supports the core DOE mission of scientific discovery and innovation. If successful, basic research into improving automated machine translation systems has the potential to impact many other

core DOE missions as well, including nuclear security, by assisting nonproliferation efforts, and energy security, by helping to ensure that foreign adversaries cannot disrupt our nation's infrastructure.

Refereed Communications:

K. Gimpel and N.A. Smith, "Quasi-Synchronous Phrase Dependency Grammars for Machine Translation," in *Proceedings of the Empirical Methods in Natural Language Processing (EMNLP)*, 2011.

Relational Decision-Making
151374

Year 1 of 3
Principal Investigator: L. E. Matzen

Project Purpose:
Computational models of decision-making traditionally require that all possible courses of action be known a priori. Extant models of decision-making hard code all of the behavioral alternatives up front and then develop an algorithm that can select the "best" option. Real-world decisions are rarely so cut and dry; often the competing alternatives and appropriate actions are uncertain, and must be deduced or constructed on the fly. According to relational memory theory, humans are able to interact with complex social networks, governments, and economies precisely because they can construct complex mental representations of events by binding the relations present in those events. Research suggests that the hippocampus is necessary for this relational binding, for memory, prediction, and imagination (Buckner 2009). This project, which will be conducted at the University of Illinois at Urbana-Champaign, draws on the RMT framework to analyze how the hippocampus represents, constructs, and manipulates complex events in real time. The project has three main phases: Phase 1: *Discovery*: two newly developed human behavioral testing methods, iPosition and the "event reconstruction technique," help us to characterize the nature of relational representations formed by intact subjects and patients with hippocampal damage when exposed to complex events involving large amounts of arbitrary relational data; Phase 2: *Analysis:* uses algorithms adapted from bioinformatics to search the data gathered in phase 1 for rich relational structure.; and Phase 3: *Synthesis:* utilizes the findings from phase 2 to implement a computational model of relational binding that can bind all manner of arbitrarily related inputs to create richly relational representation and can serve as the basis for a better model of decision-making, one that can capture a broader set of possible alternatives than any current decision-making model.

Summary of Accomplishments:
We designed two experiments to examine relational memory's contribution to complex decisions. The first of these tested how memory for spatial configurations constrains the reconstruction of spatial configurations. The second tested how memory for whole events (including temporal, spatial, and object information) influences the reconstruction of those events. In both cases, we analyzed how the choices participants made arose from the underlying relational representations. Our analysis concluded that an internal representation based on complex and arbitrary relations was more likely the source of participants' decisions than was capacity, spatial, or episodic explanations. The second study argues that relational memory demands are proportional to the complexity of the task (as indexed by the number of possible choices), and arbitrariness (as indexed by the number of choices excluded by general policies) of the task in question. The findings of the first experiment have been written and are pending submission for publication in the *Journal of Neuroscience*.

Based on the findings of these empirical studies, we designed and tested a new computational model of hippocampal anatomy, physiology, and function. This model was designed to be extremely close to the gross anatomy, microcircuitry, and neurodynamics of the hippocampus, using a nonlinear dynamical modeling method for individual neurons. Tests of this model demonstrated that, for a very wide range of the parameters, synchronous waves of firing arose automatically within the Cornu Ammonis (CA) subcomponents of the model. These synchronous dynamics are observed in just this region in the hippocampus in vivo. Further, the model demonstrated that different inputs could affect the phase of the rhythmic firing. This discovery resonates with findings suggesting rhythmic hippocampal firing provides a mechanism for binding together arbitrary compositions of stimuli, and critically, for reactivating those compositions to guide behavior.

Significance:

The proposed neural modeling work is part of ongoing research and development of technology around the "human element." A neurocognitive model of how anxiety-laden, aversive experiences affect memory and ultimately decision-making could directly benefit DOE, DoD, DHS, and other federal agencies. All of these agencies are impacted by the human element and are particularly concerned about how stress can impact decision-making.

All US government missions depend on an effective and informed decision-making process. These real-world decisions are iterative, with each choice unlocking some new options, while shutting down others. Furthermore, none of these choices involves a clear set of options, such that, frequently, the best course of action is a creative and non-obvious response that has never before been used. US government personnel use their personal expertise to gather information and create hypothetical scenarios that guide their decision-making. While there is much research on the outcomes of decision-making this extended, interactive process is much less well understood. This project makes significant progress in clarifying the extended decision-making process and provides a model for improving that process.

CVD Encapsulation of Mammalian Cells for Hazardous Agent Detection
151375

Year 1 of 3
Principal Investigator: J. C. Harper

Project Purpose:
Despite significant progress made in the last few decades towards portable and robust detection systems, biological detection devices still face major limitations. Living cell-based sensors have proven effective in addressing real-time and near-neighbor detection issues; however, relevant mammalian cell line–based sensors require frequent replenishment with new cells, and function in limited environments (stable, developed regions). To be practical for the warfighter and defense of structures in less developed regions, cell-based sensors require a functional biocompatible interface between the immobilized / encapsulated cells and the macro-world. This interface would expand the range of environments for which the sensor would be practical, and limit required technical expertise for operation.

To meet the need of robust easy-to-use threat detection systems, we are developing a chemical vapor deposition (CVD) technique designed to coat cells in silica. Preliminary results have shown this method to be effective in encapsulating Jurkat cells (immortalized T lymphocytes) in a conformal thin silica shell. Unlike methodologies based on sol-gel technology, CVD encapsulates single cells, is easily tunable, and reduces the stresses exerted on cells due to exposure to toxic byproducts. These benefits of the Si CVD system may allow for the production of cell-based systems with viabilities and activities of several weeks, as opposed to the two-day viability for the most relevant cell-based sensing line, CANARY, developed by MIT/Lincoln Labs. This advance would be a significant breakthrough making cell-based biosensors practical in a wide range of environments including unstable regions with limited infrastructure. If successful, we expect that the Si CVD method can be adapted to yeast or mammalian cell lines, further expanding the utility of cell-based sensors.

Summary of Accomplishments:
In the first year of this project, elements addressing three of the four milestones have been completed, including completion of experiments investigating the effect of chemical vapor deposition (CVD) exposure time on cell viability, and silica shell morphology and thickness. Viability and sensing activity were characterized by the ability of a cell to respond to a model analyte, galactose, and produce yellow fluorescent protein (YFP). Deposition times of 5, 20, and 90 minutes were investigated. Deposition times of 5 minutes resulted in cells with a detectable silica shell and higher responsiveness to chemical stimuli 18 days post-coating when compared to similarly aged un-encapsulated cells. Longer deposition times (> 20 min) produced a thicker shell with less-conformal morphologies, and were detrimental to long-term responsiveness. Significant effort was exerted to produce a fluorescence microscopy technique to characterize Si shell morphology and thickness. This effort was not successful; however, these measurements were effectively made using scanning electron microscopy and energy dispersive spectroscopy. This work also completed aspects of project goal: investigation of long-term viability and sensing activity of silicacoated cells.

Other achievements included the exploration of the effectiveness of one catalyst and three protectants on short-term cell viability. We showed that the catalyst poly-l-lysine, and protectants folic acid and trehalose, do not improve Si coating efficiency or cell viability. We also showed that the protectant, zentec, reacts with the silica precursor, tetramethyl orthosilicate, to produce a fluorescent signal that interferes with fluorescence-based detection.

While validating initial yeast-YFP results versus a bacterial system using an inducible beta-galactosidase reporter, it was found that the beta-galactosidase system had lower background activity, a faster response time, and is available in cell lines relevant for cell-based biodetection. Studies have been initiated with this improved beta-galactosidase reporter system.

Significance:
Our investigations over the first year of this project have already shown the importance of the initial metabolic phase for encapsulated yeast *Saccharomyces cerevisiae* cells, as well as the importance of the presence of media additives to the encapsulation matrix, on the rate of reporter gene expression, and on the long-term viability of the cells. These results elaborate on other silica gel whole-cell encapsulation studies, and provide important insights that may facilitate design and development of effective cell-based biosensors for case-specific applications.

If successful, this study will yield fundamental understanding of the requirements for interfacing biological materials with nanomaterials, and demonstrate the first successful encapsulation of mammalian cells in a silica nanostructured composite for cell-based sensing. The resulting technology will allow for development of robust chem/biosensors that will directly impact the early warning needs of DoD, Defense Threat Reduction Agency (DTRA) and DHS, prove useful in remote sensing for treaty verification for DOE, and find application in medical diagnostic technologies for the National Institutes of Health (NIH).

Refereed Communications:
J.C. Harper, D.M. López, E.C. Larkin, M.K. Economides, S.K. McIntyre, T.M. Alam, M.S. Tartis, M. Werner-Washburne, C.J. Brinker, S.M. Brozik, and D.R. Wheeler, “Encapsulation of *S. cerevisiae* in Poly(glycerol) Silicate-Derived Matrices: Effect of Matrix Additives and Cell Metabolic Phase on Long-Term Viability and Rate of Gene Expression,” *Chemistry of Materials*, vol. 23, pp. 2555-2564, May 2011.

Autotuning for Scalable Linear Algebra
151376

Year 1 of 1
Principal Investigator: M. A. Heroux

Project Purpose:
Parallel computing is an enabling technology across many science and engineering disciplines. Numerous studies have shown the impact of parallel computing and the need for further advances in computing capabilities. Future parallel computers will undergo dramatic changes in design, posing numerous challenges to application and library developers. In particular, numerical linear algebra — which represents the core computational requirements for many applications — will be impacted. New algorithms and new performance optimization techniques are required as architectures become much more complicated, and a priori hand-tuning optimization becomes infeasible. Instead, automated tuning methods — using the computer system itself as the means to achieving optimal performance — will be essential. The work of this project will leverage ongoing efforts at the University of Texas-Austin (UT-A) and at Sandia to develop automatic algorithm and software tuning, called autotuning, for computationally intensive numerical linear algebra operations.

Automatic algorithm and software tuning (autotuning) has been under investigation for several years, and its impact has been demonstrated in limited settings. However, practical use of autotuning remains elusive, while at the same time the need for it is growing. In our work, we intend to develop a systematic approach within the FLAME (Formal Linear Algebra Methods Environment [from UT-A]) and Trilinos (from Sandia) software frameworks. We will target optimal algorithms for multicore and manycore processors, including graphics processing units. By combining algorithm research with state-of-the-art software frameworks, we have a unique opportunity to deliver autotuning benefits to the worldwide application community.

Summary of Accomplishments:
We have shown that Model Driven Engineering can be successfully applied to automating performance optimization of kernels in the problem domain of dense linear algebra on distributed memory systems. The results show competitive and even superior performance over a human expert in the design of optimal computational methods.

Significance:
High performance parallel computing is an essential technology across most DOE and federal science and technology missions. Specifically, numerical linear algebra is a common core computational requirement for most of these applications. Advances in autotuning will impact the majority of science and technology application spaces across federal agencies and national laboratories.

Refereed Communications:
B. Marker, E. Chan, J. Poulson, R. van de Geijn, R.F. Van der Wijngaart, T.G. Mattson, and T. E. Kubaska, "Programming many Core Architectures — A Case Study: Dense Matrix Computations on the Intel SCC Processor," *Concurrency and Computation: Practice and Experience*, published on line, pp.1-18, 2011.

Fundamental Investigation of CVD Graphene Synthesis
151377

Year 1 of 3
Principal Investigator: M. T. Brumbach

Project Purpose:
High-quality, large-area graphene has the potential for many exciting applications. While much larger than mechanically exfoliated graphene, chemical vapor deposition (CVD) synthesized graphene does not exhibit the same quality of physical properties. However, the potential for scalability of graphene CVD processing is extremely attractive, and this is the most promising method for its commercial viability. Through this investigation of the fundamental science behind CVD graphene growth, graphene with physical properties the same as mechanically exfoliated graphene will be realized on a large and inexpensive scale. This is a collaborative effort between Sandia and the University of Texas-Austin.

Summary of Accomplishments:
When the research group at the University of Texas-Austin first published single-layer graphene synthesis on copper foils via thermal chemical vapor deposition, the individual graphene domains were only seven microns across — determined using isotope labeling. Since then, we have conducted a parametric study to determine the effects of growth temperature, pressure, and methane flow rate on the graphene domain size and nucleation density. During this study, we were able to increase the graphene domain size to 20 microns across. We then took these parameters to an extreme by utilizing copper pockets to create very low carbon partial pressure inside the pocket. This ultimately led us to be able to grow single-crystal graphene domains over 500 microns across. Trace chemical analysis was used to evaluate impurity levels of various copper substrates to evaluate the role of impurities on graphene nucleation and growth.

We also examined the effects of the copper substrate purity on the graphene domain density and growth rate. Three copper substrates were used: 1) ultrahigh-purity Puritronic grade 99.9999% copper, 2) 99.8% pure copper from Alfa Aesar which is the most commonly used substrate for CVD graphene, and 3) industrial 102 copper alloy (99.8%–99.97% copper). In order to measure the graphene growth rate, the $^{13}CH_4$:CH_4 ratio was changed every 30 seconds during growth. Because the position of the graphene Raman G-peak is dependent on this ratio, the location of the graphene deposited at various periods of growth can be mapped out. Surprisingly, the graphene coverage rate was not a function of the substrate used. Instead, other parameters such as methane flow rate and temperature must determine the coverage rate. However, the linear growth rate is strongly dependent on the copper purity: the more pure the copper, the faster the linear graphene growth.

Significance:
This research is critical to a broad range of activities relevant to DOE and national security because graphene represents a cheap alternative substrate with highly advantageous properties for solid-state devices. Several specific device-types that could benefit from a high quality, cheap conductive substrate such as graphene include sensors (defense and environment), photovoltaics (energy), LEDs (energy), transistors, and microelectronics (science). This work also provides basic science research for advancing our knowledge of important materials systems.

Probing Surface Phenomena in Elevated-Temperature Energy Materials under Realistic Conditions
151378

Year 1 of 3
Principal Investigator: W. Chueh

Project Purpose:
In one hour, more energy from sunlight strikes the earth than the amount consumed by the entire planet in one year. As the most abundant energy source, the sun must play a large role in any global-scale renewable energy conversion strategy. However, tapping into this vast resource does not come without challenges. The intermittent and geographically varying nature of solar radiation means that storage and delivery, of solar-derived energy are critical steps required for mass utilization. Chemical bonds are one of the most effective mediums for storing energy because of their high energy densities. However, despite the great potential of solar fuels, solar-to-chemical and chemical-to-electricity conversion efficiencies remain low and uncompetitive with those of conventional routes. This project will explore the novel, elevated-temperature materials that can be employed for the efficient production of solar fuel from H_2O and CO_2 (via photo/electrochemical and thermochemical dissociation) and its subsequent conversion to electricity (via fuel cells).

As most chemical reactions are thermally activated, even a modest increase in the operating temperature can produce drastic effects on the rates and reduce or eliminate the use of precious elements. To realize the benefits of higher-temperature processes, the understanding of charge and mass transport at gas-solid interfaces will be advanced using in-situ and *in-operando* techniques to probe the inner workings of state-of-the-art materials, and to use this knowledge to identify new materials that will boost energy conversion efficiencies. The project PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments:
During the first year of the project, we have conducted numerous experiments investigating the surface properties of oxide catalysts under operating conditions. Progress is as follows:

1. The surface and bulk oxidation state of cerium oxide was successfully characterized in samarium-doped ceria, a promising material for solar fuel production and fuel cells. We found that the surface is extremely stable under a wide range of oxygen pressure and temperature. Thermodynamic analysis shows that a reduced surface is stabilized entropically.

2. We have tested a number of perovskite-based fuel cell cathodes in true fuel cell environment in the ambient pressure x-ray photoelectron spectroscopy endstation at the Lawrence Berkeley National Laboratory. Preliminary data shows that high catalytic activity is associated with abundance of Co^{2+} species on the surface. Strontium oxide formation on the surface also reduces the activity of the catalyst.

Significance:
This work is directly relevant to DOE's mission to provide the science and technology to power the US without contributing to climate change. This project is developing new ways to characterize the electrochemical technologies that will be increasingly relied upon to achieve energy security by efficiently storing and converting energy.

Virus-Like Particles Displaying Random Peptide Libraries for Use in Rapid Response to Pathogens
151379

Year 1 of 3
Principal Investigator: C. E. Ashley

Project Purpose:
Virus-like particles (VLPs) are the noninfectious structural analogues of bacteriophages and viruses and have proven useful in numerous materials science and biomedical applications. VLPs of MS2 bacteriophage self-assemble from 180 copies of a single coat protein into a monodisperse, 28-nm icosahedron that is tolerant of high-density peptide display and can be rapidly loaded with nearly any cargo of interest. MS2 VLPs are well suited for use as potently immunogenic vaccines against viral and bacterial pathogens and as targeted nanocarriers capable of delivering therapeutic agents to virally infected cells with high specificity. The utility of MS2 VLPs in vaccine development and targeted delivery applications can be enhanced though their development as a platform for random peptide display, which, upon synthesis of a complex library, will enable identification of peptide sequences with an affinity for any material (e.g., monoclonal antibodies or proteins expressed by cells infected with intracellular pathogens). The goal is to develop a complex random peptide library entirely in vitro using MS2 VLPs as a display platform. In vitro VLP display is entirely novel and will enable the convenient production of high complexity libraries (10^{11}–10^{12} members), will mitigate the need for extensive purification prior to biopanning, and will make library construction and affinity selection amenable to automation. We will utilize monoclonal antibodies against viral or bacterial pathogens to affinity select VLPs capable of eliciting a neutralizing, protective antibody response. We will also identify VLPs capable of targeting virally infected cells using receptors necessary for viral entry in affinity selection experiments. To inhibit the production and spread of viruses, we will utilize targeted VLPs to deliver siRNA that induces sequence-specific degradation of viral mRNA. VLP display promises to be a remarkably powerful, universal technology that will enable rapid, cost-effective identification of vaccine candidates and targeted nanocarriers in order to effectively combat infectious disease. The project PI is a President Harry S. Truman Fellowship recipient.

Summary of Accomplishments:
During FY 2011, we made substantial progress toward achieving two of our five aims: 1) developing a VLP-based vaccine against Nipah virus (NiV), a BSL-4 paramyxovirus that causes fatal encephalitis in 70% of infected individuals and 2) developing a VLP-based nanocarrier capable of delivering therapeutic RNAs to NiV-infected endothelial cells and neurons. We have employed complex, random peptide libraries constructed by our collaborator at the University of New Mexico (UNM) to affinity select MS2 VLPs that bind to a conformational, neutralizing monoclonal antibody (mAb-26) against NiV glycoprotein G (NiV-G). The predominant sequence that resulted after two rounds of selection using a high valency vector (encodes VLPs that display 90 peptides each) and one round of selection using a low valency vector (encodes VLPs that display ~3 peptides each) was the 10-mer (10 amino acid peptide), RTSNQILRPK (arginine–threonine– serine– asparagine– glutamine– isoleucine–leucine– arginine– proline–lysine). VLPs that display a high density (90 peptides/VLP) of this peptide bind to mAb-26 with high affinity (dissociation constant = 17.8 nM) and induce a peptide-specific, high titer (> 10^4) IgG (immunoglobulin G) response when injected into C57Bl/6 mice. We have also performed affinity selections against recombinant ephrin B2 (EFNB2), a receptor expressed by host mammalian cells that mediates macropinocytosis of NiV. FSSIPWA was the predominant sequence after two rounds of selection using the high-valency vector and three rounds of selection using the low-valency vector. VLPs that display 90 copies of this peptide have a 350-fold higher affinity for HEK-293 cells (EFNB2-positive) than for CHO cells (EFNB2-negative) and are internalized by EFNB2-positive cells

via macropinocytosis. During FY 2011, we have also identified VLPs that bind to lipopolysaccharide (LPS) isolated from the model bacterial pathogen, *E. coli* O157:H7; VLPs that display 90 copies of the LPS-specific peptide, SGASFPPGFG, bind to Gram-negative bacteria 10^4-fold more effectively than to Gram-positive bacteria (e.g., MRSA [multiply resistant *staphylococcus aureus*]).

Significance:
This project has the potential to substantially contribute to the national security missions of Sandia, DHS, Defense Advanced Research Projects Agency (DARPA), and Defense Threat Reduction Agency (DTRA). Rapid, cost-effective identification of vaccine candidates capable of inducing a neutralizing immune response against arbitrary pathogens is a key thrust of our nation's biodefense efforts; our preliminary work with Nipah virus vaccines will enable us to secure funding from the National Institute of Allergy and Infectious Diseases (NIAID) and has promoted interactions with DTRA and Applied Research Laboratory (ARL). Targeted delivery of therapeutics to pathogenic bacteria or virally infected host cells will likely become a DTRA investment area within the next five years. Our work with targeting Nipah-infected cells was presented at the SMART FIT workshop, held in Springfield, VA in August 2011, and garnered great interest from Chem-Bio DTRA representatives. This work is, additionally, leveraged by a recently funded NIH Eureka grant led by Sandians, as well as faculty from the University of Illinois Urbana-Champaign, University of California San Diego, and UNM. Complex, random sequence VLP libraries are also being used to identify targeting peptides for other nanoparticle-based delivery systems being developed at Sandia; we are using nanoporous particle-supported lipid bilayers for delivery of therapeutic RNA to cells infected with intracellular pathogens. This project leverages Sandia's core competencies in materials science, nanoparticle synthesis and characterization, supported lipid bilayers, novel synthetic lipids, and hyperspectral imaging. 'VLP display' is, furthermore, being used to develop high-affinity detection reagents that recognize various chemical and biological targets, which is relevant to DARPA, DTRA and DHS. Finally, development of novel biotic/abiotic nanocomposites is achievable using VLPs as a synthesis platform and is of interest to the DOE Office of Basic Energy Sciences (BES). We are currently working with staff at the Center for Integrated Nanotechnologies (CINT) to synthesize VLP-based plasmonic nanoparticles for in vivo imaging and single-particle tracking applications.

Refereed Communications:
C.E. Ashley, E.C. Carnes, G.K. Phillips, D. Padilla, P.N. Durfee, P.A. Brown, T.N. Hanna, J. Liu, B. Phillips, M.B. Carter, N.J. Carroll, X. Jiang, D.R. Dunphy, C.L. Willman, D.N. Petsev, D.G. Evans, A.N. Parikh, B. Chackerian, W. Wharton, D.S. Peabody, and C.J. Brinker, "The Targeted Delivery of Multicomponent Cargos to Cancer Cells by Nanoporous Particle-Supported Lipid Bilayers," *Nature Materials*, vol. 10, pp. 389-397, April 2011.

C.E. Ashley, D.R. Dunphy, Z. Jiang, E.C. Carnes, Z. Yuan, D.N. Petsev, P.B. Atanassov, O.D. Velev, M. Sprung, J. Wang, D.S. Peabody, and C.J. Brinker, "Convective Assembly of 2D Lattices of Virus-Like Particles Visualized by In-Situ Grazing-Incidence Small-Angle X-Ray Scattering," *Small*, vol. 7, pp. 1043-1050, April 2011.

C.E. Ashley, E.C. Carnes, G.K. Phillips, P.N. Durfee, M.D. Buley, C.A. Lino, D.P. Padilla, B. Phillips, M.B. Carter, C.L. Willman, C.J. Brinker, J.C. Caldeira, B. Chackerian, W. Wharton, and D. S. Peabody, "Cell-Specific Delivery of Diverse Cargos by Bacteriophage MS2 Virus-like Particles," *ACS Nano*, vol. 5, pp. 5729-5745, July 2011.

High-Density Nanopore Array for Selective Biomolecular Transport
151381

Year 1 of 1
Principal Investigator: K. Patel

Project Purpose:
Although nanoscale devices have been developed to perform individual tasks, little work has been done on developing a truly scalable platform: a system that combines multiple components for sequential processing, as well as simultaneously processing and identifying the millions of potential species that may be present in a biological sample. Scalable micro and nanofluidic devices are limited, in part, by the ability to combine different materials (polymers, metals, semiconductors) onto a single chip, and the challenges with locally controlling the chemical, electrical, and mechanical properties within a micro or nanochannel. In this project, we are applying our sophisticated tools to manipulate biomolecules at their own length scale to enable new methods for chemical synthesis and detection not possible at large length scales.

In collaboration with University of Illinois at Urbana-Champaign (UIUC) through a strategic partnership, we have developed a unique construct known as a nanopore gate: a multilayered polymer-based device that combines microscale fluid channels with nanofluidic interconnects. Nanopore gates have been demonstrated to selectively transport molecules between channels based on size or charge. We will fully utilize these structures to develop new methods to actively control transport and identify biological species using a nanopore. Our metalized nanopore devices have the ability to create multiple, separate conductive connections at the interior surface of a nanopore. Our innovative approach is to: 1) use the interior electrodes for the direct sensing of biological molecules such as double stranded DNA, 2) probe the electrical potential and charge distribution at the surface of charged proteins, and 3) actively turn on and off electrically driven transport to select specific biomolecules to transit nanopores. The overall goal is to demonstrate that nanopore gate devices can utilize the nanoscale effects to solve important and challenging biological problems.

Summary of Accomplishments:
The primary focus of our research is to develop micro- and nanofluidic structures tailored for detection and identification of specific proteins and other biological molecules. These structures, referred to as molecular gates, consist of arrays of nanopores (diameters <100 nm) that connect two or more microfluidic channels. A key feature of molecular gates is that they are 3D networks of channels, rather than conventional microfluidic devices where channels are confined to a single plane. This design enables the following:

1. High-density arrays of nanopores, which allow nanoscale transport phenomena to be exploited while maintaining high throughput.
2. Specialization of each layer for a single task. The surface chemistry of channels in an individual layer can be modified without interfering with other layers, or in some cases, entirely different materials can be used.

We have designed a multilayer design that enables simultaneous parallel processing between layers. For example, a simple electrophoretic separation may be performed in one channel, while individual bands are extracted and undergo a chiral separation in another layer.

Previous designs for molecular gates relied on polymers as the primary material for both microchannel and nanopore layers. In our design, microchannels can be molded into Polydimethylsiloxane (PDMS) or etched into poly-methylmethacrylate (PMMA) and bonded to nanoporous polycarbonate membranes.

Our design offers desirable characteristics such as optical transparency and electrical isolation, the surface chemistry proves difficult to control, resulting in band broadening during electrokinetic transport and variability between devices. We have tested methods in fabricating nanoporous silicon to allow us to fabricate an all silicon/glass molecular gate. Switching over to silicon also allows more precise control of channel dimensions, since wet and dry etching techniques have been well refined over the past forty years.

Significance:
Despite this prevalence of nanostructured materials in numerous applications, relatively little is now known about the fundamental behavior of fluids and charged species within the confinement of nanoscale structures having dimensions ranging from a few to several tens of nanometers. This works will benefit many crosscutting investment areas by providing improved understanding of transport processes not just within a single nanopore but a network. This new understanding will aid rational design of storage and method to selectively transport molecules relevant to Sandia's mission. Development of molecular gates as a scalable architecture for controlling molecules and nanotransport is a vital part of DOE's mission to advance scientific understanding of nanoscale phenomena. Tools to help understand nanoscale transport will ultimately lead to the development of new diagnostic devices and methods to explore alternatives in biosciences and behavior of biomolecules, environmentally sound energy sources, and new methods for water purification.

This strategic partnership is viewed as an important step toward establishing a long-term partnership between Sandia and UIUC faculty aimed at enhancing the education of next-generation scientists and engineers and accelerating the development of innovative technologies supporting American competitiveness in the global economy.

Thermal Transport Properties of Nanostructured Materials for Energy Conversion
151382

Year 1 of 3
Principal Investigator: D. L. Medlin

Project Purpose:
Devices based on composite thin film arrays of nanostructures are of emerging interest for photovoltaic and thermoelectric energy conversion. An important factor controlling the efficiency of these devices is the thermal transport properties of the nanostructures. However, the thermal transport properties of such nanostructures are poorly understood because it is inherently difficult to measure them. Key issues of concern include contact resistance, surface roughness, equipment resolution, and processing limitations. Two important questions arise. First, how can the thermal transport properties of nanostructures be rigorously measured? Second, what are the relationships between individual nanostructure properties and the effective properties of a composite thin film?

To address these questions, we are conducting a comprehensive experimental study of the properties of nanostructured thin films and individual nanowires. We will focus on ZnO nanostructures because of the importance of this class of material to emerging thermoelectric and photovoltaic applications. We are using multiple measurement techniques, both optical and electrical, to measure the thermal transport, determining the anisotropic nature of the material properties and investigating differences between discrete nanostructures (e.g., single nanowire) and multiple, interacting nanostructures (e.g., nanowire film). The characterization of novel materials necessitates challenging, cutting-edge, adaptive measurement techniques; the development and application of these techniques will enable realization of novel energy conversion materials. The research is a collaboration with Stanford University.

Summary of Accomplishments:
We have successfully made electrical measurements of 1% Ga-doped individual ZnO nanowires and junctions between nanowires. We studied the impact of contacts on nanowire devices by varying the type of metal used to make electrical contact. Gold, titanium, and silver electrodes were patterned on nanowires using electron beam lithography. From the devices formed with Ohmic contacts, we were able to compare the resistance of a single nanowire to the resistance of a nanowire junction with the latter showing 104 times higher resistance than an individual wire. Devices with Schottky contacts formed between the metal electrode and the semiconducting nanowire demonstrated that a combination of thermionic emission and tunneling likely dominates current transport through these contacts. We created an electrothermal model for these Schottky contact nanowires devices. The model demonstrates the peak temperature rise occurs at the contact, and it correctly predicts the failure mode observed by post-measurement imaging of the devices. These results can be used to effectively design Schottky contact nanowire devices which have received extensive attention for energy harvesting and sensor applications.

We demonstrated the ability to measure the thermal properties of ZnO nanowire films using a harmonic surface heating technique. Solution synthesized ZnO nanostructures are desirable for deposition and manufacturing purposes, but the solubility of the resulting films precludes measurement methods requiring solution processing, namely photolithographic techniques. To overcome this incompatibility, we utilized a shadow mask process. We used an automated spray-coating machine to spray nanowire films of uniform thickness. After depositing a thin, electrically insulating layer of parylene and evaporating measurement structures, we made electrical contact using spring-mounted, 0.1-μm radius tungsten probe tips. Initial measurements demonstrate the ability to vary signal frequency while extracting the third harmonic voltage, thus providing surface temperature variation as a function of thermal penetration depth into the underlying film.

Significance:

Energy conversion devices based on thermoelectric and photovoltaic technologies have broad application across DOE and national security mission space. Examples include long-lived autonomous power sources, localized cooling devices, power scavenging, and waste heat recovery. The critical goal of US energy independence relies on the ability to increase the efficiency of such energy conversion technologies, rendering them competitive with more conventional technologies. This research is making important contributions to that end.

On Strongly Coupled Partitioned Schemes for Solving Fluid-Structure Interaction Problems Using High-Order Finite Element Models Based on Minimization Principles
151383

Year 1 of 3
Principal Investigator: D. Z. Turner

Project Purpose:
High-order formulations for solving fluid-structure interaction problems using the finite element method are being developed and implemented in this project. The C^0 Lagrange type, higher-order, spectral finite elements will be employed for all numerical discretizations. The solid will be modeled using a finite strain St. Venant Kirchhoff constitutive model; likewise, the laminar fluid will be described by the incompressible Navier-Stokes equations. The use of a single high-order numerical framework, namely the finite element method, will allow for enhanced compatibility and accuracy in the physical coupling of the fluid and structure. In the interest of achieving an ideal variational setting for the numerical formulation, all finite element models will be constructed using minimization principles. The solid mechanics problem will be discretized using traditional weak formulations while least-squares finite element models will be employed for the viscous fluid. Least-squares formulations will naturally avoid shortcomings associated with weak formulations of the Navier-Stokes equations, such as the inf-sup condition and the need for numerical upwinding. The viscous flow equations will be expressed with respect to an arbitrary Lagrangian-Eulerian reference frame, thus allowing for the use of a fluid mesh that evolves with time. Motion of the fluid mesh will be achieved through the use of standard pseudo-elasticity procedures. Strong coupling between the fluid and solid will be enforced using implicit strongly coupled partitioned procedures. Various relaxation, prediction, and approximate Newton methods will be employed in the context of the partitioned approach. The Schur complement method will be used to condense out all element level interior nodes from the global set of finite element equations. Overall performance of the numerical formulations will be assessed by solving benchmark problems of particular interest to Sandia. The work is in collaboration with Texas A&M University.

Summary of Accomplishments:
We have completed the implementation of his high-order finite element method in an object oriented C++ code. Initial verification work has begun and the basic principles have been extended to investigate the use of the proposed method to preserve the discrete maximum principle for diffusion type problems. This work was reported in a presentation given at the2011 *US National Congress on Computational Mechanics*.

Significance:
A significant portion of Sandia's mission space is dedicated to solving coupled problems. These include the design of re-entry systems (of interest to DOE/NNSA, DoD and National Aeronautics and Space Administration [NASA]), aeroelastic modeling of captive carry of a weapon under wing (DoD), and the design of wind turbine rotors (DOE/Energy Efficiency and Renewable Energy [EERE]). This project will support advancing the coupling among Sandia's existing code capabilities. Among Sandia codes, the maturity of individual physics modules is much higher than that of the coupled capabilities. This is due to our lack of understanding of the complexities of coupling. The proposed research will significantly advance our sophistication in this area.

Nanostructured Metal Oxide Photoelectrodes for Solar Hydrogen Production
151384

Year 1 of 1
Principal Investigator: B. R. Antoun

Project Purpose:
The efficient, widespread direct utilization of solar energy represents an important technical challenge facing the US in the twenty-first century. The ability to convert solar energy to chemical energy in the form of a storable fuel is critical in this effort. Application of photoelectrochemistry is highly attractive in this pursuit due to its versatility in using solar energy to drive chemical reactions for fuel production. In particular, the solar photoelectrochemical production of hydrogen from aqueous solutions is of fundamental importance as it could fit into a comprehensive nation-wide carbon-neutral energy infrastructure.

The critical component for implementation of photoelectrochemical hydrogen production systems is the photoactive electrode. There are immense technical challenges associated with the fabrication of efficient, stable, and low-cost materials for photoelectrodes. Photoelectrode materials must possess appropriate electronic and optical properties for solar energy conversion and electrochemical charge transfer, as well as maintain stability when irradiated and electrically biased in aqueous conditions. Metal oxides are the most important class of materials for this application due to their inherent stability during photo-excitation in aqueous conditions and their appropriate electronic band edge positions.

In order to meet these demanding requirements, fundamental research is required in the fabrication of metal oxides with complex stoichiometries as well as appropriate electrode structure on the nanoscale. This work is being conducted in collaboration with the University of California at Berkeley. Nanoscale architectures have been shown to enhance photoconversion efficiency because of the beneficial charge transport properties associated with their operation. Pulsed laser deposition is a physical vapor deposition technique uniquely suited to fabricate and study photoelectrodes for solar-driven hydrogen production. The physical mechanisms associated with laser-material interactions permit simultaneous optimization of photoelectrode structure and stoichiometry, required to increase photon conversion efficiency for the process. Through careful experimental design, one can achieve a wide variety of photoelectrode structures, which allows systematic study of chemical composition and electronic and optical properties.

Summary of Accomplishments:
We studied oxide materials for solar hydrogen production. The design and construction of numerous systems for the study of solar hydrogen production were utilized to produce several interesting new studies. These studies yielded many interesting results, which were published in peer reviewed technical journals.

Specifically, UC Berkeley produced doped, porous oxide electrodes using a laser-based physical vapor deposition. The photoelectrochemical, optical, and physical properties of the oxide electrodes were examined in detail. A separate study examined a unique heterostructure oxide material, which was fabricated and studied in a collaborative effort. Its electronic structure was studied by synchrotron-based x-ray spectroscopies at Lawrence Berkeley National Laboratory, and indicated the presence of new and technologically relevant interfacial phenomena. A third published perspective article involved a review of literature followed by original research results involving a heterostructure of iron and tungsten oxide nanomaterials.

A fourth article, which is to be published soon, outlined a new concept for the solar-driven generation of hydrogen. Several other studies are in manuscript form and will be submitted shortly to major journals.

Significance:
The solar-driven photoelectrochemical production of transportable hydrogen fuel is directly in accordance with the national security mission of DOE. It is an environmentally friendly process that only utilizes resources readily available domestically. Furthermore, upon combustion in a fuel cell, hydrogen produces only water. Therefore, the solar-driven production of hydrogen from water and subsequent electricity generation represents a closed loop and produces zero carbon emissions.

Refereed Communications:
C.X. Kronawitter, S.S. Mao, and B.R. Antoun, "Doped, Porous Iron Oxide Films and their Optical Functions and Anodic Photocurrents for Solar Water Splitting," *Applied Physics Letters*, vol. 98, p. on line, March 2011.

C.X. Kronawitter, J.R. Bakke, D.A. Wheeler, W.-C. Wang, C. Chang, B.R. Antoun, J.Z. Zhang, J. Guo, S.F. Bent, S.S. Mao, and L. Vayssieres, "Electron Enrichment in 3D Transition Metal Oxide Hetero-Nanostructures," *Nano Letters*, vol. 11, pp. 3855-3861, August 2011.

C.X. Kronawitter, L. Vayssieres, S. Shen, L. Guo, D.A. Wheeler, J.Z. Zhang, B.R. Antoun, and S.S. Mao, "A Perspective on Solar-Driven Water Splitting with All-Oxide Hetero-Nanostructures," *Energy and Environmental Science*, vol. 4, pp. 3889-3899, September 2011.

Chromophore-Functionalized Aligned Carbon Nanotube Arrays
155064

Year 1 of 1
Principal Investigator: A. Vance

Project Purpose:
We recently demonstrated the effectiveness of tuning the low intensity, visible light response of single-walled carbon nanotube field effect transistors (SWNT-FETs) through noncovalent attachment of light-isomerizable chromophores. These single SWNT devices (i.e., there was one nanotube in each device) served as excellent model systems and generated data that could be supported by theory; however, more practical devices will be based on carbon nanotube films or arrays. This project is intended to expand the utility of chromophore-functionalized SWNT devices by building devices with aligned SWNTs that fully span the interelectrode spacing (i.e., the transistor's channel). Such an arrangement would eliminate issues of resistance at SWNT junctions that would be expected in randomly oriented SWNT films, while increasing the area of the detector. Examples of aligned SWNTs have been demonstrated, but these were not utilized to examine the response of the devices to low-intensity visible light. This project is exploring the preparation and characterization of novel carbon nanotube devices that could lead to new types of nano-enabled light sensors. Aligned SWNT devices are a very recent advance in the area of carbon nanotubes, and their potential uses are only now beginning to be explored.

Summary of Accomplishments:
The project was originally divided into two parts with initial work focused on the growth of horizontally aligned SWNTs. Once these were prepared, devices would be fabricated and tested with chromophores. SWNT growth was found to be more challenging than anticipated so the project was did not proceed beyond efforts to optimize SWNT growth conditions. A growth furnace was set up with flow controllers for argon, hydrogen and methane. Variables that were adjusted to attempt to optimize SWNT growth conditions included gas flow rates, catalyst deposition methods, and growth substrates. Interesting results were obtained with e-beam evaporated iron catalyst on 1000 Å SiO_2 on <100> Si substrate. Aligned arrays of SWNTs were not obtained, but a very long SWNT was observed in scanning electron microscopy (SEM) images. Tracking the SWNT and assembling the images showed that a microns-long nanotube was produced.

Another approach utilized drop-cast iron chloride that was subsequently annealed to form iron nanoparticle catalysts. This method produced sparse, but fairly long (~5 µm) SWNTs; however, aligned arrays were not found.

Significance:
This project will benefit the national security mission of DOE by enabling the development of new, nano-enabled photodetectors. These devices may be of particular interest as infrared detectors, where carbon nanotubes may provide advantages over existing technologies. A shared vision (SV) project is under way with Lockheed Martin to explore this possibility, and while this project proposes an entirely different approach, the general area of optical detection complements the SV project. In addition, DOE's Office of Science has recently requested novel methods of photon conversion.

Time Encoded Radiation Imaging
155299

Year 1 of 1
Principal Investigator: P. Marleau

Project Purpose:
Passive detection of special nuclear material (SNM) at long range or under heavy shielding can only be achieved by observing the penetrating neutral particles that it emits: gamma rays and neutrons in the MeV energy range. The ultimate SNM standoff detector system would have sensitivity to both gamma and neutron radiation, a large area and high efficiency to capture as many signal particles as possible, and good discrimination against background particles via directional and energy information. Designing such a system is a daunting task.

Using time-modulated collimators could be a transformative technique leading to practical gamma-neutron imaging detector systems that are highly efficient with the potential to exhibit simultaneously high angular and energy resolution. We hope to demonstrate their use in an SNM detection system and add an important new tool to the radiation detection repertoire. Time modulation will have several important advantages over existing approaches to gamma and fast neutron imaging. The design is greatly simplified with time modulation as the necessary time resolution is trivially achieved. The rotating collimator modulates the signal of any detector positioned at its center. For this reason, the detection method, efficiency, size, and energy resolution of the central detector are largely decoupled from imaging.

By careful design, a collimator could be designed to effectively modulate both gammas and neutrons. A single large detector that is sensitive to and can discriminate both neutrons and gamma rays could then be used for simultaneous dual mode imaging. Time-modulating radiation detectors have seen some use in astrophysics applications, but very few investigations have addressed SNM detection. Specifically, we know of no other fission energy neutron detection technology that relies on time modulation of the signal.

Summary of Accomplishments:
The concept for this work was originally intended to extend the proof of concept established in a previous project to create a larger and more efficient imager. The target application is to detect and locate SNM at large standoff distances. Toward this goal, we designed a very large central detector; however, we quickly realized that portability constraints would greatly limit the performance of such a detector. In order to fit a rotating mask into a transportable container of reasonable size (~8 feet across), the number of mask elements that encircle the central detector would need to be constrained to achieve an aperture size comparable to the large diameter of the central detector constraining the angular resolution of the imager.

Therefore, we created a new concept that does not require large masses of shielding material. The Portable Rotating Imager using Self Modulation (PRISM) is composed of only a few detectors that rotate around each other on a common axis. The footprint and overall mass of this imager is thus reduced to the size and mass of the detectors alone.

This leads to a much more efficient and compact imager; however, the imaging properties of a passive mask are lost. There is no longer a mathematical guarantee of artifact free reconstruction, but this design allows for much more detector material in the volume allotted to the imager. Thus, for the same dwell time, the PRISM detector will collect greater statistics which may overcome its lack in image quality on a per event basis.

We, therefore, designed and constructed a detector with four large liquid scintillator elements (12" diameter by 15" depth) to field in a large standoff demonstration. We successfully demonstrated this new mode of imaging and established the detection of neutron sources to standoff distances up to 130 meters.

Significance:
National and international security collaborators in both governmental and private sectors are seeking better tools to search for radioactive threats. This new concept for a high-efficiency imaging of fast neutrons could yield dramatic improvements over existing tools for this application. This project addresses the need for technologies to aid in the protection of the US public on US soil against weapons of mass disruption.

Three-Wafer Stacking for 3D Integration
155367

Year 1 of 1
Principal Investigator: T. Bauer

Project Purpose:
Considerable technical advantage is obtained by combining separate analog, digital, and other technology functions in a single low-volume solution utilizing vertical die stacking. In a previous project, we explored and developed technologies to achieve vertical die and wafer stacking, also known as 3D Integration, with particular success in the area of stacking two layers. However, stacking three or more layers introduces additional complexities that need to be investigated. In this project, we are exploring the combination of process and integration techniques required to achieve stacking of three or more layers.

Stacking three or more die or wafers requires some means to establish electrical continuity between the layers. Through silicon vias (TSVs) are a powerful, yet elegant, solution to achieving these interconnects. We have demonstrated a robust TSV integration scheme in which TSVs that are established on the front side of a wafer penetrate deep into the wafer, and we have a notional process flow that describes how we might establish electrical contact through the back side, but the process and integration details remain to be sorted out so we can demonstrate and fully realize the benefits of vertical wafer stacking with three or more layers.

Broadly speaking, vertical wafer stacking will enable a wide variety of new system architectures by enabling the integration of dissimilar technologies in one small-form-factor package. Defining the process and integration details is critical to fully realizing vertical wafer stacking of three or more layers.

Summary of Accomplishments:
We executed the following activities:
1. We designed and procured the photolithography masks necessary to demonstrate a testable TSV technology characterization vehicle.
2. We identified, developed, and demonstrated suitable wafer thinning techniques.
3. We identified, developed, and demonstrated temporary and permanent wafer bonding techniques.
4. We developed and demonstrated techniques to reveal our TSVs.
5. We demonstrated a pad formation process.

Significance:
Vertical stacking will enable a variety of new system architectures, including the integration of dissimilar materials and integration of commercial parts with parts of our own manufacture in a single, small-form-factor unit. This can result in significant improvements in functionality, cost, reliability, and schedule for “next level” microsystems assemblies that would benefit national security applications including cryptography, communications, high-performance computing, and data processing in severe environments. This year’s activities have advanced our capability because we have demonstrated that we can thin wafers to expose through silicon vias “in-house,” with excellent uniformity. Prior to this year, we sent wafers to external vendors for thinning. This is potentially problematic because wafers of our own manufacture are often export controlled material and releasing the wafers to an external vendor carries an element of risk. Also, we now have a mask set that allows us to develop and practice the unit operations required to demonstrate through silicon vias, with a testable structure, so that we can conclusively evaluate performance and yield. These capabilities are key to a variety of sensor and computational technologies important to DOE and other national security agencies.

Thermal Spray Integration of Electronic Components
155403

Year 1 of 1
Principal Investigator: P. G. Clem

Project Purpose:
This project performed printing of strain gauges on composite wind turbine blades as a method for real-time performance enhancement, damage monitoring, and state of health assurance. Currently, high failure rates of wind turbines is one concern for fielded devices, and commercial turbine blades are not instrumented — a wind speed sensor is often mounted on the turbine nacelle, but there is no real-time detection of blade tip deflection, strain state, or vibration level. This work developed high-speed (millisecond response speed) printed strain gauges directly on manufactured wind turbine sections for real-time feedback.

Summary of Accomplishments:
This project achieved the following major objectives:

- functional strain gauges were printed on composite wind turbine blades, and processing temperatures and times were found that produced high-performance strain gauges without degradation of the wind turbine blade composites
- strain gauge performance was tested, and found to be linear out to 4000 microstrain (0.4% strain levels), consistent with in-field strain states
- methods for real-time data telemetry at data speeds up to 1 kHz were developed and tested
- a methodology for integration of this technology with current SMART (SMART BLADE GmbH) adaptable aerodynamic turbine blades was found, and a proposal developed to extend this work further to a fielded wind farm prototype

Significance:
This work maps to DOE goals in alternative energy and innovation: strategic theme 1: energy security, goal 1.1 energy diversity and strategic theme 3: scientific innovation and discovery. We anticipate that this research will develop new Sandia capabilities of use to alternative energy, aircraft nondestructive evaluation, and other national security applications.

Low-Loss Fiber-Waveguide Coupling for Silicon Photonics Integrated Circuits
155407

Year 1 of 1
Principal Investigator: A. L. Lentine

Project Purpose:
Many silicon photonic integrated circuit applications have performance or power dissipation reduction limited by their insertion losses. The losses are comprised of fiber-to-waveguide coupling losses, active device losses, passive waveguide loss, and polarization splitter and rotator losses. We have demonstrated several world-class research results in silicon photonics, among them, the lowest power 4 fJ (40 μW) 10 Gbps modulators, the first full C-band tunable filters, fast (2.4 ns) reconfigurable switches, novel high-sensitivity thermal sensors, and low V-pi Mach-Zehnder broadband 10 Gbps modulators. These devices had 20-dB fiber-to-fiber insertion loss, primarily because of the high fiber-to-waveguide coupling loss. Also, the devices were measured using a probe station with special lensed fibers. Both the loss level and the lack of packaged devices are impediments to realizing the potential of the technology in applications and, in some cases, are impediments to securing research funding. The goal of this research is to demonstrate fiber-to-waveguide coupling losses below 1 dB per interface in a technology compatible with our silicon photonics modulators, switches, and passive waveguide devices.

The goal of the project is to design a fiber-to-waveguide interface compatible with our silicon photonics platform. Creating such a low-loss interface requires a detailed understanding of the underlying physics of wave propagation between the fiber and waveguide modes. We expect to develop unique structures and insights into the design of the waveguide transition region between the fiber and silicon photonic waveguides for the active devices.

Summary of Accomplishments:
We performed a comprehensive investigation of end-coupling of single mode fibers into silicon photonics waveguides.

Significance:
Silicon photonics is a technology potentially applicable to a wide variety of national security problems. Applications include low-power communications for high-performance computing, fighter aircraft, and satellites, thermal imaging, inertial navigation, and RF signal processing.

Exploring the Origin and Applications of Extraordinary Electromagnetic Transmission
155410

Year 1 of 1
Principal Investigator: H. Loui

Project Purpose:
This project seeks to investigate the phenomenology of extraordinary electromagnetic transmission (EEmT), and its applicability in furthering the capabilities of our nation's electromagnetic sensors. The science and technology (S&T) questions we are seeking to answer in this project are as follows: What are some of the theoretical explanations governing this newly observed phenomenon? Do they adequately explain its origin? Can they be explored to allow an array of subwavelength elements to radiate efficiently? These questions have not been thoroughly addressed by the scientific community that discovered EEmT, whose experimental work showed that periodic arrays of subwavelength apertures in metal plates, which should not have permitted the transmission of electromagnetic radiation of much longer wavelength, indeed did transmit this radiation.

The extrapolation from EEmT results to its potential utilization in sub-wavelength ultra-compact sensor arrays has not been explored in open literature. A majority of the work that deals with sub-wavelength antenna elements focuses on how to make an electrically small antenna element radiate more efficiently, not an electrically small antenna array made up of sub-wavelength antenna elements. Our idea is novel but counter intuitive, so was EEmT.

The difference between existing EEmT experiments and our proposed work lies in sensor excitation — the former focused on scattering and transmission through passive perforated metal plates by a pre-existing radiated electromagnetic wave in free space. Our questions open up the possibility of direct excitation and efficient detection of long-wavelength signals at sensor arrays having elements much smaller than the operating wavelength. This feat was previously believed to be impossible, as was EEmT. We will attempt to prove otherwise by investigating EEmT using physical intuition, analytical analysis, electromagnetic simulation, and experimental testing. Our conjecture, if true, could revolutionize the capabilities of pre-existing electromagnetic sensors, giving our nation cutting-edge detection capabilities and the element of surprise in combating terrorism.

Summary of Accomplishments:
- We explored the origins of EEmT for both periodic and single, cut-off apertures in metal plates illuminated by plane wave and excited by propagating waveguides.
- We learned that in the case where cylindrical apertures in a periodic array are evanescent or cutoff, EEmT is caused by mutual coupling between the apertures external to the hole. Exotic explanations using surface-plasmon polaritons (SPP) and diffraction anomalies are unnecessary for perfect electric conductor (PEC) structures.
- We discovered EEmT in arrays of evanescent apertures fed by propagating waveguides. The evanescent apertures act as a narrow band distributed matching network between the connected waveguides and air — a phenomenon not observed for an isolated element.
- We demonstrated means for EEmT resonances to be lowered further in frequency (making it even more extraordinary).
- We showed, using large-scale time-domain simulations, that EEmT transmission through a single subwavelength hole with surface bull's eye corrugations is due to field enhancement at the mouth of the aperture via constructive surface wave interference. This field enhancement or focusing effect offsets the attenuation associated with the evanescent aperture and produces EEmT.

- We carried out various numerical EEmT experiments using patch arrays and discovered anomalous resonances due to mutual coupling.

Significance:
This research furthers our understanding of subwavelength-radiator physics. It opens up the possibility of making multiple inefficient radiators radiate efficiently through engineered mutual coupling which may enable controlled EEmT operation of ordinary arrays. An active array operating in the ordinary electromagnetic transmission (OEmT) mode may be configured to operate in the EEmT mode where reception and transmission of wavelengths much greater than the array spacing occurs with reduced bandwidth and gain; essentially, this entails operating the entire array efficiently as a single element or multiple subelements. Our work benefits intelligence, surveillance, and reconnaissance for the improvement of national security by enabling electrically small, high-powered, efficient, and covert electromagnetic sensor arrays.

Exploring Energy Transfer Processes in Semiconductor Light Emitters
155411

Year 1 of 1
Principal Investigator: M. H. Crawford

Project Purpose:
Solid-state lighting, based on light-emitting diodes (LEDs), could have dramatic impact, including a 10% reduction of US electricity consumption. To realize this impact, LED efficiencies must be advanced to 50% or more. While LEDs are inherently single-color emitters, solid-state lighting further requires high-quality white light. To date, the dominant approach to LED-based white lighting employs a blue LED to optically pump green/yellow and red phosphors. This multistep approach suffers from numerous processes that limit efficiency, including light extraction from the blue chip, incomplete light absorption in the phosphor, and scattering losses in the phosphor. Present-day red phosphors also have broad emission into the deep red, where eye response is poor, further limiting luminous efficiency. A key challenge is reducing the losses inherent in optical pumping while finding an alternative to low-performing phosphors.

We propose a novel concept to overcome these challenges, namely nonradiative mechanisms such as Forster-type dipole-dipole interactions for transferring energy from a blue LED to secondary emitters. In addition to eliminating losses inherent in optical pumping, our approach would replace traditional phosphors with semiconductor nanocrystals to provide tunable, narrow-linewidth emission necessary for high-quality and high-efficiency white light. The goal of this research is to develop integrated LED-nanocrystal design concepts compatible with these novel energy transfer approaches.

The proposed approach is an innovative departure from radiative energy transfer approaches that are presently employed and attacks the most critical roadblocks to solid-state lighting, namely energy efficiency and white color quality. However, realization of the proposed nonradiative energy transfer introduces significant challenges. For example, the requirement of only a few nanometer separations of the LED active layer and the nanocrystal emitter necessitates entirely new designs of LED p-n junctions and nanocrystal integration approaches.

Summary of Accomplishments:
The primary design concept that we explored in this project was the use of naturally formed hexagonal pit defects (“v-defects”) to integrate quantum dots with InGaN quantum well LED structures. Specifically, if we could demonstrate effective quantum well deposition on the sidewalls of the pit defects, or alternatively maintain high quality quantum wells intersecting the pit wall, and loaded these pits with nanocrystalline quantum dots, the nanometer-scale proximity of dots and wells might enable efficient energy transfer via dipole-dipole interactions. One accomplishment was proving the ability to control the density and depth of v-defects in the InGaN LED material. These characteristics were controlled via growth conditions during deposition of the LED layers. A second accomplishment was establishing the highest density of v-defects that could be sustained without significant degradation of LED performance. We found that densities as high as 10^9 cm^{-2} were acceptable to maintain device performance whereas 4 x 10^9 cm^{-2} dislocation density yielded notable degradation of LED output power and efficiency. Finally, we discovered p-type layer designs and growth conditions to maintain the pit to the surface of the LED such that quantum dot integration is feasible. Transmission electron microscopy studies revealed that further work is needed to optimize sidewall epilayers for efficient energy transfer.

Significance:
The energy challenge the world will face in the coming century is widely recognized as one of the most grave and pressing missions of the DOE. Energy-efficient solid-state lighting, once it is widely adopted, will reduce US electricity consumption by 10%, saving ~$25B/year, and reduce the need for generating capacity by 50 GW, or 50 large nuclear reactors. The energy transfer processes under investigation in this project could lead to a lighting technology with improved efficiency, color quality and flexibility. Novel designs to enable these processes could impact other energy-related technologies, such as solar photovoltaics.

Confined Cooperative Self-Assembly and Synthesis of Optically and Electrically Active Nanostructures
155412

Year 1 of 1
Principal Investigator: H. Fan

Project Purpose:
There has been a widespread interest in self-assembly and synthesis of molecular building block (MBB)-based ordered arrays aiming to emulate natural light harvesting processes and energy storage (e.g., biomacromolecules: porphyrins) and to develop new nanostructured materials. However, technologies that leverage the structural advantages of individual MMBs have not been fully realized and have been limited by synthesis method. In this project, we are pursuing a facile, cooperative, self-assembly synthetic method using amphiphilic surfactants or block polymers and functional MBBs, aiming to synthesize new classes of highly ordered active nanostructures. We plan to amplify the intrinsic advantages of individual MMBs by engineering them into well-defined 1D to 3D nanostructures. Cooperative noncovalent interactions — assisted self-assembly of amphiphilic surfactants and MBBs — will be utilized to form well-defined "micelle-like" nanostructures. Driven by intermolecular interactions, subsequent nucleation and growth confined within these nanostructures will lead to formation of 1–3D ordered optically and electrically active nanomaterials with structure and function on multiple length scales. At the molecular level, MBBs provide well-defined structure and unique optical and electrical property. On the nanoscale, controlled assembly of MBBs enables formation of ordered nanostructures with precisely defined size, shape, and intermolecular arrangement of the individual MBBs, which will facilitate intermolecular charge or energy transfer or delocalization. On the macroscale, ordered arrays of these nanostructures allow easy device fabrication for investigating synergetic optical/electrical properties to correlate structure-property relationships.

Summary of Accomplishments:
We discovered a surfactant micelle-confined self-assembly solution process to synthesize 1D nanoporous, ordered porphyrin nanostructures with well-defined external morphologies. One-dimensional nanostructures include nanowires and nanorods with controlled diameters and aspect ratios. This facile and versatile aqueous solution process assimilates photoactive macrocyclic building blocks (porphyrin) inside surfactant micelles, forming stable single-crystalline high-surface area-frameworks with well-defined external morphology defined by the building block packing. The nanostructures were characterized using transmission and scanning electron microscopy, x-ray diffraction, N_2- & NO-sorption isotherms, thermogravimetric analysis, UV-vis spectroscopy, and fluorescence imaging and spectroscopy. The nanostructures are monodisperse and may further assemble into hierarchical arrays with multimodal functional pores. The nanostructures exhibit enhanced optical properties over the individual chromophores. The nanostructures were demonstrated to photo-catalytically reduce platinum (Pt) to form Pt nanoparticles or 3D nanoparticle networks with controlled thickness templated on the nanostructure surface.

Significance:
Leveraged by Sandia's pioneered technologies in self-assembly of nanoparticles, this project will lead to new materials for fundamental research aimed at a better understanding the chemical and physical phenomena that occur during charge or energy transfer processes, for addressing issues associated with photovoltaics, chemical and biological sensors, and energy storage, which directly impacts DOE and national security missions.

The biomacromolecule nanocrystals exhibit unique structures and optical/electrical properties for new sensor and energy storage device integrations. Understanding structure and properties of these well-defined (model) nanomaterials will provide key knowledge to design and engineer materials for optimized optical and electrical performance. Leveraged with the Center for Integrated Nanotechnologies' (CINT) capabilities, the success of this proposal directly impacts DOE/Sandia's missions in Energy, Homeland Security, and Defense.

Refereed Communications:
F. Bai, Z. Sun, H. Wu, R.E. Haddad, X. Xiao, and H. Fan, "Templated Photocatalytic Synthesis of Well-Defined Platinum Hollow Nanostructures with Enhanced Catalytic Performance for Methanol Oxidation," *Nano Letters*, vol. 11, pp. 3759-3762, 2011.

Electrokinetic Measurements of Surfaces
155553

Year 1 of 2
Principal Investigator: B. Simmons

Project Purpose:
Despite the ubiquity of hydrophobic colloids and the importance of hydrophobic micro/nanodevice substrates, generally accepted descriptions of electroosmotic phenomena that provide predictive capability at hydrophobic surfaces are lacking. Models and descriptions of these systems are often contradictory, and those models that do agree with each other have not, to date, offered detailed predictions. The long-term goal of this project with Presidential Early Career Awards for Scientists and Engineers recipient, Brian Kirby, at Cornell University is to characterize the dynamic effects of nanobubble formation and decay on electrokinetic system response in polymer-water systems and use this knowledge to enable rational design of micro/nanofluidic devices with hydrophobic interfaces. The overall objective of the research is to characterize both the microscopic (nm) and macroscopic (μm) effects of nanobubbles produced at hydrophobic interfaces upon solvent or temperature cycling, with specific attention to nanobubble stability as a function of shear and transverse electric field. We will combine: a) electrokinetic measurements at hydrophobic interfaces, b) techniques for controlled formation of surface nanobubbles, and c) atomic-force microscopy of surface interfaces so as to identify 1) the thermodynamic parameters that define the charge processes at hydrophobic surfaces, 2) the role of gas bubbles on electrokinetic transport, and 3) the effect of shear and electric field on nanobubble stability. Our central hypotheses are that the interplay of nanobubbles in electrokinetic phenomena is tied to the size of the bubbles as compared to double-layer shielding and that electrokinetically induced shear will decrease the characteristic time for nanobubble decay by overcoming diffusion-limited transport of dissolved gas.

Summary of Accomplishments:
In the past year we have designed, constructed, and implemented a flat plate streaming potential cell. The cell was designed in Pro/E and machined from a combination of polycarbonate and aluminum. The polycarbonate forms the inner part of the cell — a small amount of the surface is wetted forming reservoirs at the up and downstream ends of the cell. The aluminum pieces, in conjunction with 1=4-20 hardware, form a clamp to seal the polycarbonate pieces. Aside from machining the polycarbonate and aluminum pieces for the direct use by the streaming potential cell, several other support structures were designed and built. These pieces are used to cut out gasket and spacer shapes from silicone and teflon.

Fixturing of pressure, flow, and voltage input/monitoring was accomplished by boring small holes in 8-32 nylon screws and inserting the appropriate conduit. For flow, a ground 16-gauge needle was pressed into the hole, forming a seal. For voltage, a platinum wire was epoxied in a similar hole; the same gluing technique was used to insert a small gauge steel tube to measure pressure. A pressure test was executed to determine the maximum sealing pressure by the cell, and was found to be in the neighborhood of 100 psi, well above the maximum pressure at which the device is to be run. A new differential pressure transducer was implemented. Also, the streaming potential device was connected to a syringe pump and labview, and data collected for plain glass slides. This polarization leads to a change in the local permittivity through a saturation effect where, once the water molecules become fully aligned in a strong field, the permittivity is unable to increase and the electric field is perturbed only slightly in the regions of alignment.

Significance:
This research ties to Sandia's mission to ensure the security and sustainability of our water resources. By developing unique capability to characterize electrokinetic effects in microsystems, the work will inform engineering design of cyclic oflefin polymer microstructures used to analyze environmental and drinking water. The fundamental insights gained by this effort support DOE goals for scientific discovery and innovation.

Refereed Communications:
V. Tandon and B.J. Kirby, "Ambient Pressure Effects on the Electrokinetic Potential of Zeonor-Water Interfaces," *Journal of Colloid and Interface Science*, vol. 361, pp. 381-387, September 2011.

Quantifying Significance of Spatial-Temporal Climatic Indicators
155650

Year 1 of 1
Principal Investigator: S. A. McKenna

Project Purpose:
The central question addressed in this project is the following: can regions of an image or a map that are anomalously high or low be reliably identified within available climate-related data products? This question is complicated by several factors, including various means of defining "significant", the inherent noise in the climatic indicator estimates, and the effects of the statistical problem of multiple comparisons in identifying significant anomalies. Estimates of climatic indicators are formulated as outputs of regression models evaluated at thousands of locations to form a map of estimated rainfall (e.g., rainfall amounts have some relation to elevation, distance from the ocean and latitude, etc.). Examination of the resulting map for areas of extremely high or low rainfall amounts that are statistically significant is complicated by spatial and/or temporal correlation of the model errors and the large number of statistical tests necessary to evaluate every location. These complications can result in false classification of anomalous regions.

Developments made over the past decade in the analysis of neuroimaging data, particularly toward improved analysis of functional magnetic resonance imaging (fMRI) and positron emission tomography (PET) scans for human brain activity may offer a solution to anomaly detection in climatic data. These techniques are being applied in this research on a continental scale and extended where necessary to work with climatic indicator data. These approaches have not previously been applied to anomaly detection in climatic and meteorological processes. Intended results of this work include faster and more accurate identification of the onset of drought conditions and techniques for the quantitative assessment of impacts of climate change on local regions.

Summary of Accomplishments:
We developed a practical approach to anomaly detection in spatial-temporal data sets that is based on statistical parametric mapping and uses the properties of truncated Gaussian fields to determine the significance of observed anomalies. This approach was successfully tested on simulated data with known anomalies of varying size, shape, and strength. We then obtained a spatial-temporal data set with weekly global satellite coverage of normalized difference vegetation index (NDVI) at a 15 x 15 km resolution for the past 30 years. Analysis of two tropical regions, Amazon Basin and Southern India, was performed in two different ways. In the first approach, regression models were used to identify anomalous times and regions based on the previous 40 weeks of observations. In the second approach, average NDVI values obtained during four El Niño years were compared to average NDVI values obtained during four La Niña years. Results show that average NDVI values in El Niño years in both regions are significantly lower than during La Niña years. This significant decrease in the vegetation indices may be a contributing factor to recently reported increases in civil conflict within tropical countries during El Niño years.

Significance:
This work directly addresses two Department of Energy Strategic Goals — namely Scientific Discovery and Innovation and climate change science. The proposed work represents a significant leap in the application of technology developed in one specific field (neuroimaging) to solve a problem in an unrelated field (climate change science).

Multivalent Interactions with Charged Lipids
156434

Year 1 of 1
Principal Investigator: S. Rempe

Project Purpose:
Multivalent ions are useful in industry and medicine, but their toxic effects pose a threat to public health. For example, in the defense industry, the multivalent beryllium (Be) ion is used in metal, oxide, and alloy forms for manufacturing nuclear components, electronic devices, high-temperature ceramics, and structural components in satellites and space shuttles. In medicine, the multivalent gadolinium (Gd) ion is widely used as a contrast agent in magnetic resonance imaging (MRI) studies. At the same time, Be is listed as a class A Environmental Protection Agency (EPA) carcinogen and poses a major occupational hazard that causes chronic inflammation in the lungs (berylliosis), whereas more and more patients undergoing MRI tests intravenously receive large amounts of chelated Gd, which partially escapes into the body and wreaks havoc with immune responses. A bottleneck in developing therapeutic options to treat inflammatory and immune disorders arising from metal ions is the lack of knowledge about how multivalent ions interact with cells. Traditional views assign toxicity of multivalent ions to their ability to displace calcium (Ca) ions in protein binding sites. In light of known effects of metal ions on the electrostatics and lateral packing of phospholipids, the major component of cell membranes, we propose an alternative hypothesis. Multivalent ions may disrupt cells at the level of the membrane by outcompeting with calcium at phospholipid binding sites, thus affecting lipid recognition by specific receptors important to inflammatory and immune responses.

To probe our hypothesis that multivalent ions displace calcium at phospholipid binding sites, we have applied our recent theoretical advances in statistical mechanics coupled to quantum descriptions of atomic interactions to explore ion selectivity in representative phospholipid binding sites. Our approach augments experimental methods that lack resolution needed to identify ion binding sites and enhances conventional molecular dynamics simulations, where force fields cannot describe polarized electron densities that occur with multivalent ion interactions.

Summary of Accomplishments:
In collaboration with membrane experts from the University of Maryland and colleagues from the University of New Orleans, we performed molecular dynamics simulations to examine solvation interactions of Na, Ca, and Gd with anionic phospholipids: 1) dioleyl phosphatidylserine (DOPS), and 2) the soluble headgroup analog, ortho-phosphoserine (mono-anionic OPS). We discovered that free Gd in solution is surrounded by 8 waters. In OPS and DOPS, we found that Gd solvation is characterized by binding to both carboxylic and phosphate groups, typically engaging two or three residues with similar sets of coordination patterns. Coordinated Gd liberates 3.5 waters from its first hydration shell to the bulk, thereby providing strong entropic driving forces for binding to the lipid. Furthermore, we found that trivalent Gd has long residence times (> 40 ns) in most binding configurations due to linking of multiple phosphatidylserine (PS) headgroups into clusters. Detailed analysis of the phase structure of various ions interacting with OPS, using ab initio methods, demonstrated the importance of induction and charge transfer effects in modeling ion-lipid binding. These analyses further confirmed that formation of neutral coordination complexes of Ca with OPS lead to aggregation and the onset of colloidal solution behavior. We analyzed Gd coordination patterns by soluble OPS and lamellar DOPS. The similarity between coordination patterns for the soluble PS compared to lamellar bilayer indicate that membrane-restrained phosphoserine groups of DOPS adjust readily to the ion. We found that Gd binding to lamellar DOPS leads to an 8% reduction of average area per headgroup, substantial changes in the lateral pressure profile in the bilayer and slight re-orientation of the headgroups. We concluded

that the altered electrostatics and pressure distribution of the ion-restructured DOPS appear to be major factors affecting the function of membrane-embedded proteins and surface receptors important to cell signaling in immune and inflammatory responses.

Significance:

The insights gained about how multivalent ions interact with and restructure the major lipid component of cell membranes is important to assessing the consequence of industrially and medically relevant ions to cell function. DOE and DoD are interested in mechanisms of cell toxicity due to ions used in manufacturing nuclear components, satellite components, and electronic devices important to the defense industry. The National Institutes of Health (NIH) has published calls for studies of the impact of metal ions in cell biology. These insights also enhance our understanding of cell signaling mechanisms because signaling initiates with reactions involving membrane-embedded proteins, whose function is determined in part by membrane properties. Greater understanding of cell signaling mechanisms can be used to guide development of therapeutics for controlling innate immune responses to pathogens important to biodefense and inflammatory responses important to public health. New collaborations established between Sandia and cell membrane experts from the Biology Department of the University of Maryland, and between Sandia and developers of simulation force fields from the University of New Orleans should lead to new discovery opportunities involving cellular membranes.

Unpublished Summaries

For information on the following FY 2011 LDRD Projects, please contact the LDRD Office:

Laboratory Directed Research & Development
Sandia National Laboratories
Albuquerque, NM 87185-0123

Project Number	Title
130711	Information Systems Analysis using Agent Collectives
130806	Material Development for Radiation Hardness
141596	Investigating Payloads and Missions for CubeSat Systems
141598	Remote Laser Location and Identification
141600	Localized Ion Radiation Effects
141601	Low Level Control Systems Assessment
141608	Self-Consuming Structural Composites
141683	Advanced Gas Transfer Systems Technology
141690	Nanoparticle Based Filler for Neutron Generator Epoxies
142540	Surety Portal
151170	A Model-Based Approach for Detection and Avoidance of Subversion in System Development Tool Chains
151360	Multi-Phase Laminates: A Study of Prompt Transformations in Abnormal Environments
151273	Nephelae: Harnessing the Cloud
151274	Static Current Measurement of FPGA Devices
151279	Localized Die Thinning for F/A of Advanced CMOS Designs
151280	Chip-Scale Datacom Component Design
151281	Remote Identification and Characterization of Advanced Materials using Hyperspectral Imaging
151284	Automated Severity Assignment for Software Vulnerabilities
151330	Pathways Toward Laser Hardening Via Systematic Characterization
153237	Enhanced Target Imaging and Reconnaissance in Multipath-Rich Environments
153888	Beam Adaptable Sonar System (BASS)
154273	Beam-Enhanced Electrical “Fingerprinting” of Complex Integrated Circuits
154693	Reliable PUFs for Supply Chain Assurance
154778	Advanced Encryption Applications

154532	Detection of Identifiable Data
155300	Behavioral Modeling of Network and Physical Transactions for the Detection of Insider Activity
156250	Assessing Vulnerabilities of Reconfigurable Logic RF Systems
157910	Authorship Attribution for Natural Language Text and Software

Appendix A: FY 2011 Awards and Recognition

Award Description	LDRD Contribution
R&D 100 Award *R&D Magazine*: Microresonator Filters and Frequency References	Project 131305, "Featureless Tagging Tracking and Locating," and others
R&D 100 Award *R&D Magazine*: Biomimetic Membranes for Water Purification	Project 117795, "Computational and Experimental Platform for Understanding and Optimizing Water Flux and Salt Rejection in Nanoporous Membranes"
2011 Federal Lab Consortium Mid-Continental Region Award for Excellence Technology Transfer: Microsystems-Enabled Photovoltaic Cells	Project 141519, "Greater-Than 50% Efficient Photovoltaic Solar Cells"
Asian American Engineer of the Year: *Pin Yang*	Project 141690, "Nanoparticle Based Filler for Neutron Generator Epoxies"
2011 DOE Early Career Research Award: *Daniel Sinars*	Project 141537, Nanoparticle Based Filler for Neutron Generator Epoxies," and others
2011 Innovation Award - Society for Laboratory Automation and Screening: *Kamlesh Patel*	Project 142042, "RapTOR: Rapid Threat Organism Recognition"
Polymer Physics Prize - American Physical Society: *Gary Grest*	Project 93529, "Nanoparticle Flow, Ordering and Self-Assembly," and others
2010 International Prize for Water Prince Sultan Bin Abdulaziz: *Darin Desilets*	Project 120208, "Cosmic-ray Hydrometrology for Land Surface Studies"
2011 Young Investigator Award - Gordon Research Conference on Photosynthesis: *Aaron Collins*	Project 141528, "From Benchtop to Raceway: Spectroscopic Signatures of Dynamic Biological Processes in Algal Communities"
2011 Akzo-Nobel Student Award - American Chemical Society: *Lauren Zarzar*	Project 141704, "Nature versus Nurture in Cellular Behavior and Disease," and others

President's Award for Merit: International Society of Logistics	Project 141588, "Leveraging Information between Heterogeneous Modeling and Simulation Tools"
Defense Programs Award of Excellence: Magneto-Raleigh-Taylor Experiments Team	Project 141537, "Stability of Fusion Target Concepts on Z"
American Chemical Society Fellow: *Tina Nenoff*	Project 141618, "Novel Room Temperature Synthesis of Nuclear Fuel Nanoparticles by Gamma-Irradiation" and others
American Chemical Society Fellow: *Ellen Stechel*	Project 131303, "Reimagining Liquid Transportation Fuels: Sunshine to Petrol"
Fellow of the Geological Society of America*:* *Peter Swift*	Project 141668, "Radionuclide Transport from Deep Boreholes"
Best Paper Award - 2011 IEEE Intelligence and Security Informatics: *Richard Colbaugh and Kristin Glass*	Project 141682, "Web Sensor," and others
Green Photonics Award – International Society for Optics and Photonics SPIE: *Gregory Nielson, et al.*	Project 141519, "Greater-Than 50% Efficient Photovoltaic Solar Cells"
First Prize Undergraduate Student Poster - 22nd Rio Grande Symposium on Advanced Materials: *R. Castillo, et al.*	Project 141704, "Nature versus Nurture in Cellular Behavior and Disease," and others
First Prize Poster Competition – American Vacuum Society: *D. Padilla, et al.*	Project 141076, "Responsive Nanocomposites," and others
Best Poster Award – Eighth International Conference on Complex Systems: *A.M. Duda and S.E. Levinson*	Project 141531, "Neurological Simulations for Emerging Brain Maps"
2011 Best Poster Award –NNSA TriLab LDRD Symposium: *Rekha Rao*	Project 141508, "Multiscale Models of Nuclear Waste Reprocessing: From the Mesoscale to the Plant Scale"

Appendix B: FY 2011 Project Performance Measures

Measure	Number of FY 2011 Projects
Refereed Publications	278
Other Communications	570
Technical Advances	126
Patent Applications	64
Post-Doctoral Researchers	93
New Staff Hired from Post-Doctoral Research	23
Awards	21

APPENDIX C: FY2011 MISSION TECHNOLOGY AREAS

Benefiting Mission Area	Number of 2011 LDRD Projects
DOE/Nuclear Security	222
DOE/Energy Security	159
DOE/Scientific Discovery and Innovation	271
DOE/Environmental Responsibility	31
Homeland Security	180
Department of Defense	200
Other Federal Agencies	97
Industry	48