Laboratory Name: Pacific Northwest National Laboratory
B&R Code: KC020102

FWP and/or subtask Title under FWP:
Defects and Defect Processes in Ceramics

FWP Number: 18048

Program Scope:
Experimental and computational approaches are integrated to develop fundamental understanding and predictive models of defects, kinetics of defect processes, and role of defects in the evolution of nanostructures and phase transformations. Ion channeling, electron microscopy, and optical and X-ray spectroscopies are used to characterize defects, defect formation under irradiation, and evolution of structural changes. *Ab initio*, molecular dynamics and kinetic Monte Carlo methods are used to model defects, defect migration kinetics, and nanostructural evolution.

Major Program Achievements (over duration of support):
Basic understanding, new data analysis models and predictive models of defect processes and irradiation damage in covalent and ionic ceramics over multiple scales. Quantified ionization-induced recovery processes in ceramics. Developed new interatomic potentials for GaN, $ZrSiO_4$, and UO_2, and computational models for recrystallization in SiC and for thermo-mechanical properties of GaN nanotubes and nanowires. Determined electronic stopping power of ions in ceramics and identified deficiencies in current models.

Program impact:
Provided globally-adopted scientific understanding, models, displacement energies, and interaction potentials for defects and irradiation effects in ceramics. Provided predictive models applicable to ion-irradiation effects, long-term storage of actinide waste forms, and performance of nuclear materials. Improved computer simulation methods for radiation effects in ionic materials. (CY05-07: 78 peer-reviewed journal articles; 1 peer-reviewed book chapter; 2 peer-reviewed conference papers; 3 edited conference proceedings, 35 invited presentations)

Interactions:
Experimental Studies – R.C. Ewing, L. Wang (Univ. Mich.); L.A. Boatner (ORNL); H.J. Whitlow (Univ. Jyväskylä, Finland); G. Possnert (Uppsala Univ., Sweden); P. Sigmund, (Univ. S. Denmark); M. Ishimaru (Osaka Univ., Japan)
Computational Studies – L.R. Corrales (Univ. Arizona); C. Meis, A. Chartier, J.-P. Crocombette (CEA-Saclay, France); M. Posselt (Research Center Rossendorf, Germany); J. Du (Univ. N. Texas); J.D. Gale (Curtin Univ., Australia); Z. Wang, H. Xiao (Univ. Elect. Sci. & Tech. of China); D. Duffy (Univ. Coll. London)

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
W.J. Weber – *Fellow*, Amer. Assoc. Advance. Science (2006); PNNL *Chester L. Cooper Mentor of the Year Award* (2006); Chair/Co-Chair, Intern'l Confs. on *Rad. Effects in Insulators* (2005), *Comp. Simul. Rad. Eff. Solids* (2006), and MRS Symp. *Growth, Modification, & Analysis by Ion Beams at the Nanoscale* (2005); Principal Editor, *J. Mater. Research* (2002-2008); Editorial Board, *Nucl. Instrum. Meth. Phys. Res. B*. (2003-2008)
R. Devanathan – Chair, MS&T Symp. *Rad. Effects in Mater.* (2006), MRS Symp. *Multiscale Modeling of Mater.* (2006), and MRS Symp. *Mater. Innovations for Next Generation Nucl. Energy* (2007); Invited, Natl. Acad. of Eng. *Frontiers of Engineering* Symp. (2005) and German-American *Frontiers of Engineering* Symp. (2007)
Y. Zhang –*PECASE* (2006); DOE-SC *Early Career Sci. & Eng. Award* (2006); Chair, MS&T Symp. *Ion Beam Modification and Synthesis in Solids* (2006); Guest Professor, Peking University (2007-2008)
F. Gao – Sci. Prog. Comm. 14th Conf. *Semiconducting & Insulating Mater.* (2007); Co-Chair (2007-2008), 9th Conf. *Comp. Simul. Rad. Eff. Solids* and 4th MMM Conf. Symp. *Multiscale Modeling of Rad. Eff. in Materials*
W. Jiang – Editorial Board, *The Open Materials Science Journal* (2007-2009)

Personnel Commitments for FY2007 to Nearest +/- 10%:
W.J. Weber (40%), R. Devanathan (50%), Y. Zhang (20%), F. Gao (30%), W. Jiang (70%), I.-T. Bae (post doc, 100%), Z. Rong (post doc, 70%), J. Yu (post doc, 10%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $825k **FY06 BA** $959k **FY07 BA** $909k

Laboratory Name: Pacific Northwest National Laboratory
B&R Code: KC020105

FWP and possible subtask under FWP:
Chemistry and Physics of Ceramic Surfaces

FWP Number: 10122

Program Scope:
This program focuses on the growth and electronic, optical, magnetic and surface chemical properties of monolithic crystalline and nanoporous amorphous transition metal (TM) and complex oxide films. Thin film growth methods include plasma assisted molecular beam epitaxy, pulsed laser deposition, metal organic chemical vapor deposition and reactive ballistic deposition. Of particular interest are the effects of electronic and magnetic dopants on the functional properties of oxide films.

Major Program Achievements (over duration of support):
(1) International scientific leadership in the growth of crystalline oxide film surfaces for fundamental investigations of surface structure and reactivity.
(2) Definitive investigations of the measurement, formation and modification of valence and conduction band offsets at epitaxial oxide – silicon interfaces.
(3) Paradigm-shifting insights into the detailed causes of room-temperature ferromagnetism in magnetically doped transition metal oxide epitaxial films.

Program impact:
Work on both monolithic crystalline and nanoporous amorphous oxide films enabled pioneering studies of a wide range of physical and chemical properties, not only at PNNL, but also in the laboratories of collaborators who have received films deposited here. The science pursued in this program simply was not possible prior to development here of the suite of oxide film growth capabilities currently operational at the laboratory. In FY 2007, this program produced 19 invited presentations, 3 invited articles, and 16 peer-reviewed publications.

Interactions:
Daniel Gamelin (University of Washington); Juerg Osterwalder (University of Zürich); Charles Ahn & Victor Henrich (Department of Applied Physics, Yale University); Marija Gajdardziska-Josifovska & Carol Hirschmugl (Dept. Physics, UW-Milwaukee); Darrell Schlom (Department of Materials Science and Engineering, Penn State University); Mike Toney (Stanford Synchrotron Radiation Laboratory); Steve Heald & Dave Keavney (Argonne National Laboratory-APS); Elio Vescovo (Brookhaven National Laboratory); Berand Jonker (Naval Research Laboratory); Andy Kellock (IBM Almaden Research Laboratory).

Recognitions, Honors and Awards (at least partly attributable to support under this program):
S.A. Chambers: E.W. Muller Award, Fellow AVS, Advisor for NSF MRSECs at Yale and UCSB, Program Chair for the 5th International Workshop on Oxide Surfaces in 2007.
G.J. Exarhos: President-Elect of the AVS, AVS Publications Chair, IUVSTA Councilor and Trustee, North American Editor of VACUUM , Fellow (ACerS, AVS, AAAS).
B.D. Kay: DOE/BES Council of Chemical Sciences, BES Materials Sciences Division Committee of Visitors, Fellow (AVS, APS, AAAS); Editorial Board Member (Progress in Surface Science, Journal of Physical Chemistry), 2007 Chairman of American Chemical Society Physical Chemistry Division.
Z. Dohnalek: 2008 Chair of PNW Chapter of the AVS.

Personnel Commitments for FY2007 to Nearest +/- 10%:
S.A. Chambers (40%), T.C. Droubay (30%), Z. Dohnalek (20%), B.D. Kay (20%), G.J Exarhos (10%), T.C. Kaspar – postdoc (100%).

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $589k **FY06 BA** $577k **FY07 BA** $727k

Laboratory Name: Pacific Northwest National Laboratory
B&R Code: KC020105

FWP and/or Subtask Title under FWP:
Molecularly Organized Nanostructural Materials

FWP Number: 12152

Program Scope:
Tailored nanoscale architectures are derived using an array of bottoms-up solution templated growth, molecular condensation, and post growth modification strategies, designed to manipulate the kinetics of coupled molecular assembly/disassembly reactions under hydrothermal conditions. Structural evolution is probed by means of molecular spectroscopy for both closed and open systems as a function of processing parameters. The ubiquitous regio-specific interfacial reactivity of carbohydrate-based natural products provides patterned templates on which ordered nanostructures grow. Structural and chemical characterization utilizes magnetic resonance spectroscopy and diffraction measurements that are complemented by electron microscopy and scattering approaches.

Major Program Achievements (over duration of support):
(1) Metal and metal alloy nanoparticles form on hydrothermally treated cellulose nanocrystals by surface-induced reduction producing oriented particles oriented along the pyranose oxygen sites of the aligned cellulose molecules.
(2) An innovative xenon polarizer has been designed and constructed that facilitates high sensitivity, temperature dependent, continuous flow hyperpolarized (HP) ^{129}Xe NMR measurements. Resident pore structure and pore inter-connectivity are evaluated in void composite architectures by means of temperature-dependent NMR measurements.
(3) Hydrothermally treated aqueous sugar and chemically functionalized sugar solutions form homogeneous carbon nano-spheres by an intramolecular condensation mechanism that invokes hydrophobic phase partitioning.
(4) Structural manipulation (cyclization, catenation) of molecular foldamers evaluated by in situ dynamic NMR.
(5) Surfactant directed mineralization of natural carbohydrate materials (wood, bamboo, rice hulls,…) precisely replicates the attendant structure over all length scales.

Program Impact:
- Operando proton and hyperpolarized xenon NMR measurements are key to understanding flow processes and water partitioning in polymer membranes which govern energy conversion efficiency in PEM fuel cells.
- Based upon wood mineralization studies, porous carbohydrate structures are manipulated to form ordered, high surface area materials that show remarkable catalytic activity or enhanced binding for toxic material sequestration.
- Manipulation of both intra- and inter- molecular forces at interfaces alters the kinetics of coupled structure-forming reactions that generate predictable structural nuances during formation of hierarchically ordered architectures.
- 39 Journal articles, 3 book chapters, 3 edited proceedings, 15 invited talks, 2 patents (FY05-07).

Interactions:
Internal—Fundamental Science Directorate, Environmental and Molecular Sciences Laboratory, Institute for Interfacial Catalysis; Materials Science Division; Environmental Technology Directorate (PNNL).
External—NRC-Canada (HP ^{129}Xe NMR porosity studies), Univ. of Utah (^{129}Xe NMR polarizer); WSU (molecular self-assembly), PSU (CP-MAS Solid State NMR & theoretical simulations); Tennessee Community College (carbon nanosphere formation); Brown University (closed system carbohydrate dehydration); SNL (Templated Growth).

Recognitions, Honors and Awards (at least in some part attributable to support under this program):
G.J Exarhos (Society Fellow - ACerS, AVS, AAAS; Editor, VACUUM; AVS: President Elect; Publications Chair; Launched Biointerphases Journal; IUVSTA: Councilor, Trustee; DOE National Mentoring Award).
W.D. Samuels (Chair, Local ACS Section); L.-Q. Wang (Editorial Board Member, Open Energy and Fuels Journal).
A.D-Q Li (Beckman Young Investigator Award, NIH General Medicine GM RO1 Award).

Personnel Commitments for FY2007 to Nearest +/- 10%:
G.J. Exarhos (40%), W.D. Samuels (20%), Y. Shin (40%), L.-Q. Wang (50%), A. DeQuan Li (WSU) (20%)

Authorized Budget (BA) for FY05, FY06, FY07:
FY05 BA $ 732k **FY06 BA $** 693k **FY07 BA $** 650k