SURFACE AND MICROANALYSIS SCIENCE DIVISION
FY 2004

MISSION:

As part of the Chemical Science and Technology Laboratory at NIST the Surface and Microanalysis Science Division serves as the Nation's Reference Laboratory for chemical metrology research, standards, and data to:

- Characterize the spatial and temporal distribution of chemical species; and
- Improve the accuracy, precision, sensitivity, selectivity, and applicability of surface, interface, microanalysis, and advanced isotope measurement techniques.

The Division provides the tools for the Nation's measurement communities to enhance U.S. industry's productivity and competitiveness, assure equity in trade, and improve public health, safety, environmental quality, and national security. We perform research to:

1. Determine the chemistry and physics of surfaces, interfaces, particles, and bulk materials, and their interactions with a broad spectrum of analytical probes including electrons, photons, ions, atoms, and molecules;
2. Determine the chemical and isotopic compositions, morphology, crystallography, and electronic structure at scales ranging from millimeters to nanometers;
3. Determine the energetics, kinetics, interactions, and effects of processes occurring on solid surfaces and interfaces as well as within materials and devices;
4. Develop and certify key Standard Reference Materials and Standard Reference Data.

ORGANIZATIONAL STRUCTURE:

The Division is organized into three groups with focused technical expertise and research in a range of CSTL program areas. The Division also benefits from the presence of two NIST Fellows who, although not associated with specific groups, interact extensively with a broad cross section of the Division and with organizations internal and external to NIST.

Microanalysis Research Group

- Performs research, develops analytical methods, and applies a wide variety of microbeam analysis techniques for the chemical, morphological, and crystallographic characterization of matter down to the nanometer length scale.
- Advances analytical techniques that primarily utilize excitation beams of electrons and X-rays to generate a signal that yields elemental, morphological, and molecular information.
- Develops improved methods of quantification and analytical modeling as well as Standard Reference Materials and Data for a wide variety of industry applications that use:

    - Scanning electron microscopy
    - Electron probe microanalysis
    - Analytical electron microscopy
    - Scanning Auger microprobe
    - Micro X-ray fluorescence
    - X-ray Photoelectron Spectroscopy
- Investigates chemometric methods in applied analytical problems involving multivariate and multicomponent systems.

Analytical Microscopy Group

- Conducts research on the chemical and structural properties of matter by applying various ion and photon based microscopies whose resolution range from micrometers to nanometers.
- Researches the fundamental aspects of the excitation process, quantification, standards development, instrumental improvements, and data analysis challenges associated with these analytical methods.
- Conducts research on autoradiography and nuclear track methods.
- Conducts research in generation and size-calibration of particles.
- Develops and applies methods for the concentration, separation, and isotope measurement of trace atmospheric gases and particles.
- Researches fundamental aspects of trace detection of explosive and narcotic particles using ion mobility spectrometry.
- Applies analytical microscopy methods to problems in materials science, semiconductor technology, biotechnology, and environmental science that use:
    - Secondary ion mass spectrometry by
        - Ion microscopy
        - Time-of-flight
        - Laser Desorption
    - Optical microscopy
    - X-ray diffraction

Surface and Interface Research Group

- Develops and applies surface and interface sensitive diagnostics involving laser-based sources, and proximal probes with high spatial and spectral resolution.
- Characterizes mechanisms of energy transfer, structures of complex interfaces, and the chemical reactivity of solid-solid, solid-liquid, and solid-vacuum interfaces
- Develops and applies advanced measurement methods to critical problems in semiconductor, polymer, electronic, photonic, and nanoscale science that use:
    - Scanned probe microscopy
    - Near-field microscopy
    - Linear and non-linear spectroscopies of nanoscale interfaces
    - Laser-based vibrational and electronic structure probes
    - Directed and self-assembled nanoscale structure

DIVISION PROJECTS

The Division plays a central role in four of the CSTL Programs: Microelectronics (MicroE), Forensics and HLS (FHLS), Industrial and Analytical Instruments and Services (IAIS), and Technologies for Future Measurements and Standards (TFMS). The Division also plays a supporting role in several other CSTL program areas: Health and Medical Products/Services (HMP/S), Environmental Technologies and Services (ETS), Pharmaceuticals and Biomanufacturing (P&B), International Measurement Standards (IMS), and Biomaterials (BMTLS). The Division technical efforts are aligned under Projects that cross-cut the scientific expertise within the Groups. The Division Project areas described below provide an indication of the technical focus areas, and the links to CSTL Program areas that are supported in each project area.

1. Spatially Resolved Chemical Characterization of Optoelectronic and Semiconductor Systems

Electronic and advanced materials are increasingly impacted by compositional changes on the submicron length scale. This is routinely seen in the semiconductor area where the ever-shrinking size of device features continues to allow the industry to realize Moore's Law – the exponential increase in transistor density on a chip. Current Division efforts span thin-film characterization, surface chemical growth mechanisms, and novel nanostructures for the electronics industry. Increased interest in optoelectronics can be seen in the activities of this program, with increased efforts being directed toward the development of measurement techniques that address needs which range from those of the Semiconductor Industry Association (SIA) roadmap to the determination of contaminants in starting materials and finished products. Activities this year that support the CSTL Program in Microelectronics span silicon-oxynitride dielectric ultrathin films, coatings, ion implant standards for surface analysis, and improved electron microprobe and optical procedures for layered specimens and thin films:

- **M.L. Walker, L.J. Richter and T.P. Moffat** (855*): In-Situ Characterization of Additives Governing Copper Electrodeposition. (*MicroE)
- **T. Jach, J.A. Small, and D.E. Newbury***: Improved Energy Stability in the NIST Microcalorimeter X-ray Detector. (*MicroE), (FHLS) (IAIS)
- **R. B. Marinenko, D.B. Klinedinst, L.J. Richter, D.S. Simons, S. Turner, J. A. Small, E.B. Steel, and F. Stevie** (North Carolina State University): *Chemical Characterization of SiGe Single Crystal Specimens and SiGe Films on Silicon with Electron Probe Microanalysis. (*MicroE)
- **E.S. Windsor, J.G. Gillen, P. H. Chi, D.S. Bright, and J. Bennett** (International SEMATECH)**:** *Characterization of Silicon Semiconductor Electronics Using SIMS Backside Depth Profile Analysis. (*MicroE)

2. Advanced Probes for Nano-Scale Chemical Characterization

The need for improved spatial resolution currently limits the ability of Industry to answer key questions regarding the chemical composition of surfaces and interfaces. Needs range from improved chemical and structural diagnostics to phase identification and trace compositional analysis. In addition to meeting current industry needs in these areas,

there is a continuing demand for new measurement methods to be developed that will be positioned to meet emerging measurement challenges. The Division develops measurement tools that enable the chemical characterization (elements, isotopes, and molecules) at millimeter to nanometer spatial scales with major, minor, and trace concentrations. We strive to develop measurement tools such that the 'microspatial' relationships of chemical species can be correlated with specific macroscopic properties.

With our relocation into the AML complete, several new instruments have been procured to expand our measurement capabilities, including a focused ion beam and a next generation AEM. The addition of these tools to the suite of instruments already housed in the AML will enable chemical characterization of nanoscale structure with increased sensitivity and spatial resolution. The scope of our current nanoscale metrology efforts can been seen in recent efforts in electronic and optical structures. These systems present an exceptionally rich area of future metrology needs, in terms of device characterization needs, novel structures that can be incorporated into metrology tools, and new chemical sensing structures. Division efforts have been applied to synthesis and characterization of novel structures and the application of surface sensitive spectroscopies to these structures. The Division has leveraged its strong capabilities in scanned probes, electron microscopy, non-linear optical methods, and photoemission in collaborative efforts with MSEL, PL and other Divisions within CSTL. Efforts this year in the CSTL *Technologies for Future Measurements & Standards* Program have led to:

- **B. Nikoobakht** and **S.J. Stranick:** *Horizontal Growth and In Situ Assembly of Oriented Zinc Oxide Nanowires.* (TFMS), *(*MicroE)
- **C.D. Zangmeister** (836)**, S.W. Robey,** and **R.D. VanZee** (836)*: Controlling "injection barriers" into prototype molecular wires through substrate coupling chemistry.* (TFMS), (MicroE)
- **L.J. Richter, M.C. Gurau,** and **D.M. DeLongchamp** (854): *Optical Characterization of Organic Electronic Thin Films* (TFMS), (MicroE)
- **J. D Batteas, J.C. Garno,** and **C.D. Zangmeister** (836): *Nanofabrication of Test Architectures for Molecular Electronics Applications* (TFMS), (MicroE)

3 - 5. Chemical Characterization of Materials

Division efforts span numerous challenges in measurement science. These may be in the area of small particles, reactions of surface layers of atomic dimension, or minor isotopics that are found in environmental samples. To sustain our position in credible measurements in such vanishingly small samples, the Division invests resources in a range of efforts to provide appropriate quality control and quality assurance capabilities of interest to U.S. industry. Our efforts aid industry in achieving ISO 9000 certification requirements, and provide the basis for traceability among the national and international standards bodies, industries and governments.

Particle measurement issues play a prominent role in this program as they arise in industrial, environmental, and processing environments. Providing appropriate

measurement tools for different particle analysis issues is a key focus in the Division. Within this program, we direct our efforts to:

i. Identify samples, contaminants, or analyze particles in advanced materials.
ii. Apply infrastructure measurement capabilities to characterize actinides and other materials.
iii. Develop standards, data, and measurement protocols for quality assurance.
iv. Transfer measurement capabilities to user communities, e.g., DoD, DoE, DHS and IAEA.
v. Characterize individual particles and populations of particles.
vi. Automate particle measurement methods, while developing or extending software for data collection, visualization, and interpretation.

Characterization of surfaces and interfaces demands methods that can address the chemical and structural changes that occur in different environments. Surface reactions are central in the area of catalysis, solid-state sensors, adsorption, and electronic device fabrication. The Division provides measurement tools, fundamental data, and models that address the events that occur at surface and interfaces during basic chemical reactions. Systems of concern include the growth and structure of thin-films and interfaces, and the formation and structure of buried interfaces. These efforts are grouped under three Division projects. Efforts under these projects primarily impacted the CSTL *Industrial and Analytical Instruments and Services* Program.

3. Chemical Characterization: Powders and Particulate Matter

- **R.A. Fletcher, G.A. Klouda** and **J.G. Gillen**: *Production of Uniform Particle Standards Using the Vibrating Orifice Particle Generator and Quantification by Optical Particle Sensor.* (FHLS), (IAIS)
- **R.M. Verkouteren** and **J.G. Gillen**: *NIST Trace Explosive Vapor Preconcentrator (EVAP) Test Facility.* (FHLS)
- **G.A. Klouda, R.A. Fletcher** and **J.G. Gillen:** *Portal Filter Particle Collection Efficiency Using Mondispersed Aerosol.* (FHLS)
- **N.W.M. Ritchie**: *A new Monte Carlo application for complex sample geometries. (*MicroE), (FHLS), (IAIS)
- **J.A. Small, N.W.M. Ritchie,** and **J.M. Davis**: *Quantitative analysis of submicrometer particles in the Scanning Electron Microscope (SEM) utilizing the ζ factor approach.* (FHLS), (IAIS)

4. Chemical Characterization: Surfaces and Interfaces

- **C.M. Mahoney, P. Yu** (SUNY at Buffalo), and **J.A. Gardella Jr.** (SUNY at Buffalo)**:** *Cluster SIMS Depth Profiling in Polymeric Blends for Protein Drug Delivery Applications.* (FHLS)
- **C.J. Powell** and **A. Jablonski** (Institute of Physical Chemistry, Warsaw, Poland): *Effects of Backscattered Electrons on the Analysis Area in Scanning Auger Microscopy. (*MicroE), (FHLS), (IAIS)

5. Chemical Characterization: Analytical Tools for High-Throughput Experimentation

- **J.G. Gillen, R.A. Fletcher, J.R. Verkouteren, R.M. Verkouteren** and **G.A. Klouda:** *Advanced InkJet Printing Technology for Trace Explosives Standards.* (FHLS)
- **D.S. Bright** and **D.E. Newbury:** *Rapid searching of spectrum image databases for rare events, or finding the needle in the haystack when you don't even know you're looking for a needle! (*MicroE), (FHLS), (IAIS)
- **J.H.J. Scott:** *XML for Microanalysis* (FHLS), (IAIS)

6. Environmental Chemical Metrology

Isotopic distributions can provide significant information about the sources of nanoscale samples that would be difficult, if not impossible, to obtain using other methods. Examples of the utility of such information ranges from ^{13}C and ^{14}C in aerosol emissions, ^{18}O in drinking water, ^{29}Si in meteorites, and enriched uranium in IAEA swipe samples. Division efforts are concentrated on improving the detection limits for isotopic methods, advancing methods for the discrimination of background signals, and the developing protocols to address interfering signals. The Division develops procedures and provides tools to measure isotopic ratios of chemical species in processes such as combustion, in atmospheric gas-particle interactions and transformations, and in contaminant transport. Efforts this year have led to:

- **R. D. Holbrook** and **P.C. DeRose** (839): *Detection of Trace Anthropogenic Contamination in Aquatic Ecosystems using Fluorescence Excitation-Emission Matrix Spectroscopy*
- **G.A. Klouda, J.J. Filliben** (898) ***and*** **H.J. Parish** (SRI International): *Reference Material (RM) 8785 Air Particulate Matter on Filter Media*

ANNUAL HIGHLIGHTS

Significant efforts during FY04 were focused on final preparation for, and the actual relocation of, all Division activities to the **Advanced Measurements Laboratory**. The move began at the end of March 2004 and the relocations of offices and laboratories were essentially complete by the first week in May. By late August, the vast majority of the instruments were operational. The Division is positioned to benefit from state-of-the-art environmental controls, with significant improvement in temperature stability, air born particulate count, and vibration isolation. Improvements in instrument performance are already noted in our SIMS effort and in the Auger efforts, with additional improvements anticipated in the other instrumentation to follow. In spite of the significant staff time that was required to prepare our instruments for the relocation and the effort required to bring the instruments back on line, the Division has maintained highly productive efforts in its key program areas.

Relocation of the Division in the Advanced Measurements Laboratory has been accompanied by and expanded involvement in metrology for **Nanoscale Science and Engineering**. During FY04 Division staff members participated in the organization *of the NNI Interagency Workshop on Instrumentation and Metrology for Nanotechnology* that was held at NIST in January 2004. This workshop brought together a cross section of industrial, academic, and government leaders who collective identified key challenges that will need to be addressed as aspects of nanotechnology move into national and international commerce. This Division authored the section of that report on "Instrumentation and Metrology for Nanocharacterization". The Division also helped Organize the "Third International Workshop on Nanoscale Spectroscopy and Nanotechnology", NASA Tech Brief's Nano 2004, and the NIST-NASA Workshop on SWCNTs: Purity and Dispersion. Furthermore, the Division helped organize industry-focused meetings in this area including the *NanoCommerce* 2003 that was held in December 2003. Division staff have also been active in the NNI-Chemical Industry Consultative Board for Advancing Nanotechnology (NNI-ChI CBAN) trough the Environmental Safety and Health (ESH) working group. Within this working group, Division staff played an active role in the drafting of the document "Recommended Topics for R&D Activities: Measurement/Detection of Nanomaterials" which is currently being distributed by NNI-ChI CBAN for consideration by several government agencies for inclusion in their R&D programs. In addition the Division also participates in the Interagency Working Group on Nanotechnology Environmental and Health Implications (NEHI) under the NNI Subcommittee for Nano Science Engineering and Technology (NSET). These and similar efforts assist in keeping Division efforts in nanoscale characterization in tune with national needs assessments.

Changing National Priorities have led the Division to embark on a major effort in support of **Homeland Security**. FY 2004 witnessed a further shift of our activities into measurement science associated with the detection and characterization of explosive particles. This effort spans all three groups in the Division, and includes efforts in particle collection, particle detection, and reference materials for the assessment of commercial technologies used for explosive particle detection.

Current aviation security legislation requires the unprecedented utilization of trace explosive detection systems for screening of baggage, cargo and passengers at US airports in support of Homeland Security. The Division is responding to the growing metrology requirements for trace explosive screening by leveraging our existing expertise in particle technology and microanalysis, analytical chemistry and chemical microscopy to build a measurement infrastructure for the continued development, characterization, calibration and standardization of trace explosive detection devices. In addition, we are developing the specialized measurement expertise that will be needed to support the next generation of explosive detection equipment. Of particular interest for both of these goals is the analysis of individual airborne explosive particles collected by trace explosive detection portal (TEDP) systems currently being evaluated by the new Transportation Security Administration (TSA) for the noninvasive and rapid identification of airline

passengers (also cargo containers and luggage) who may be carrying or were exposed to explosives. Portal systems rely on the removal, collection and preconcentration of particles that are dislodged from the passenger as they pass through the portal device.

It is vital to study the fundamental interactions of individual explosive particles with various collector surfaces to determine the operational characteristics of these devices, to achieve the highest possible detection sensitivity, and to minimize false positives. In close consultation with the TSA Trace Explosives Detection Group, three key areas of research were identified where NIST could have a significant impact on continued development and deployment of this emerging technology. Key areas of focus for this work include: (1) exploration of methods to improve the sampling and collection efficiency of explosive particles, (2) a complete microscopic and chemical characterization of individual explosives and their degradation behavior, (3) the development of calibration procedures and standards for explosive particle detection.

The Division continues its effort to provide measurement support for international safeguards programs. In the fall of 2003 a staff member participated in the *IAEA Consultants Group Meeting on Particle Analysis for Safeguards* in Bruyers le Chatel, France. At this meeting, Division efforts on *"New Research, Software-Features, Isotopic Calculations, and Support Issues" were presented.* This is part of an ongoing Division effort to support the metrology issues that underlie IAEA efforts in monitoring worldwide nuclear nonproliferation.

The Division in involved in several **Competence Projects** that were funded by the NIST Director. FY04 marked the fourth year of funding for both the *Molecular Electronics* and the *Polymer Thin Films: A Testbed for Combinatorial Methods* projects. The former is a joint effort with the Process Measurements and the Physical and Chemical Properties Divisions of CSTL and the Semiconductor Electronics Division of EEEL, and is showing impressive progress as the participants merge computational chemistry, scanned probe measurements, two photon photoemission, and molecular electronic test structures to realize metrologies appropriate for future systems that incorporate molecular scale electronics. The Combinatorial Methods effort combines the development of multispectral probe capabilities within the Surface and Microanalysis Science Division and gradient library methods in the Polymer Division. These efforts are rapidly approaching the anticipated merger of multispectral probes with assessment of libraries generated using gradient techniques. In FY04 the Division initiated the competence project *3D Chemical Imaging at the Nanoscale* that brings together existing expertise from the Electron and Optical Physics Division in PL, the Metallurgy Division in MSEL, ITL, and our Division to build measurement capabilities that will move existing 2D capabilities to the third dimension, while increasing spatial resolution and chemical contrast, while reducing data acquisition times. FY05 will mark the beginning of two additional Competence projects, with a joint effort *Metrology to Enable the Realization of Organic Electronics Devices* that involves MSEL and EEEL, and the project *SuperResolution, In-situ Microscopies for Characterization of Nanostructured Materials* that is joint with PL. These forward-looking projects point to the interactive nature of

Division staff, as they develop metrology to meet anticipated areas of need.

STAFF RECOGNITION:

David Simons – received the **Justin C. French Award** with Robert R. Greenberg (839) and Richard M. Lindstrom (839) in recognition of their development and critical evaluation of an instrumental neutron activation analysis method for the determination of arsenic in silicon, and transferring this technology to the semiconductor industry's chip fabrication lines through their development of a series of Ion Implant in Silicon Depth Profiling SRMs.

David Simons - was elected a **Fellow of the American Vacuum Society** (AVS) in recognition of his development of ion implanted standard reference materials for advanced semiconductor metrology.

Edgar S. Etz – received the **Edward Bennett Rosa** Award with S.J. Choquette (839), W.S. Hurst (836), and D.H. Blackburn (Guest Researcher) for development of SRM 2241 through 2244, a suite of Raman intensity correction standards that will, for the first time, enable U.S. industry to accurately intercompare data acquired from widely differing instruments.

Cynthia J. Zeissler – received the **Department of Commerce Bronze Medal** for her contributions in advancing the state-of-the-art of using fission tracks in solids for detection of fissionable elements such as uranium. These developments have been of exceptional benefit to other federal agency programs in nuclear materials analysis.

C.M. Mahoney, S.V. Roberson, and J.G. Gillen were nominated for the CSTL Technical Achievement Award in FY 2004. Their paper " Depth Profiling of 4-Acetamindophenol-Doped Poly(lactic acid) Films Using Cluster Secondary Ion Mass Spectrometry" Anal. Chem. **2004,** 76, 3199-3207 reported on the feasibility of using cluster secondary ion mass spectrometry for depth profiling of drug delivery systems. The behavior of various biodegradable polymer films under dynamic SF_5^+ primary ion bombardment was investigated, including several films doped with model drugs. The results show that, for some drug delivery devices, it is possible to monitor the distribution of a drug as a function of depth by using cluster primary ion beams.

INTERACTIONS:

The Division is involved in advisory and technical efforts with other government organizations including EPA, IAEA, NSF, TSA, NIH, DHS, and DoD. Close relations are maintained with national (e.g., ASTM, ANSI, MAS, EMSA, NFPA) and international (e.g., ISO, IUPAC, IAEA, VAMAS) organizations. The Division also maintains extensive interactions with private industry including: ATDF (Advanced Technology

Development Facililty - a subsidiary of SEMATECH), Charles Evans & Assoc., Dow Chemical, Dow Corning, DRI, DuPont, ExxonMobil Chemical, General Electric, GMA Industries Inc., Honeywell, Ionoptika. Landauer Inc., McCrone Assoc., MicroFAB Technologies, Inc, Noran, Phase 3 Imaging Systems, Peabody Scientific, Pfizer, Photon Imaging, Schafer Vallecitos Laboratories, Syagen, SRI, 3M, Visteon, and XOS, Inc.

SELECTED TECHNICAL ACTIVITIES

Title: Horizontal Growth and *In Situ* Assembly of Oriented Zinc Oxide Nanowires

Authors: B. Nikoobakht and S. J. Stranick

Context: Research in the area of nanoscopic materials has the potential for providing new classes of materials with performance and functionality not achievable by systems on large length scales. In the field of photonics, work is underway in the development of nanoscale light sources and detectors that are capable of operation at the single photon level. When coupled with the ability to manipulate and assemble these elements into hierarchical structures, nanodevices capable of performing sophisticated functions such as quantitative chemical measurement will be realized. Our recent efforts in this area have focused on developing methods for directed growth and assembly of semiconducting nanowires (NW). In this work, an approach has been developed which promotes the horizontal growth, *in situ* alignment, and predictable positioning of ZnO NWs. This strategy allows for the large scale production and assembly of ZnO NWs and NW arrays.

Major Accomplishments: In the majority of semiconductor NW syntheses schemes, a thin catalyst film is used as nucleation site/media for growth of NWs, resulting in standing NWs with diameters ranging from 20-120 nm. However, this approach has limited control over the diameter of the NWs making diameters smaller than 10 nm difficult to prepare. Perhaps more important for most device applications, NWs need to be assembled and aligned in the plane of the surface. To this end, we have developed a new technique for the growth of semiconductor NWs which overcomes the limitations stated above. Using our approach, single crystal NWs with adjustable diameters between 1-20 nm are grown horizontally (in the plane of the surface) along crystallographic directions on an *a*-plane sapphire surface. Our studies show that the crucial requirements for horizontal growth of NWs are the size of and the spacing between Au catalyst nanodroplets. To fulfill these geometric requirements, we have used thin Au lines (width < 200 nm) and/or lines of Au nanoparticles as nucleation sites for NWs growth (Figure 1a). Using a vapor phase transport process at high temperature, each nanoparticle in the Au lines nucleates ZnO formation and becomes a NW. Figure 1 shows an example of the resulting oriented, NW arrays formed using this procedure.

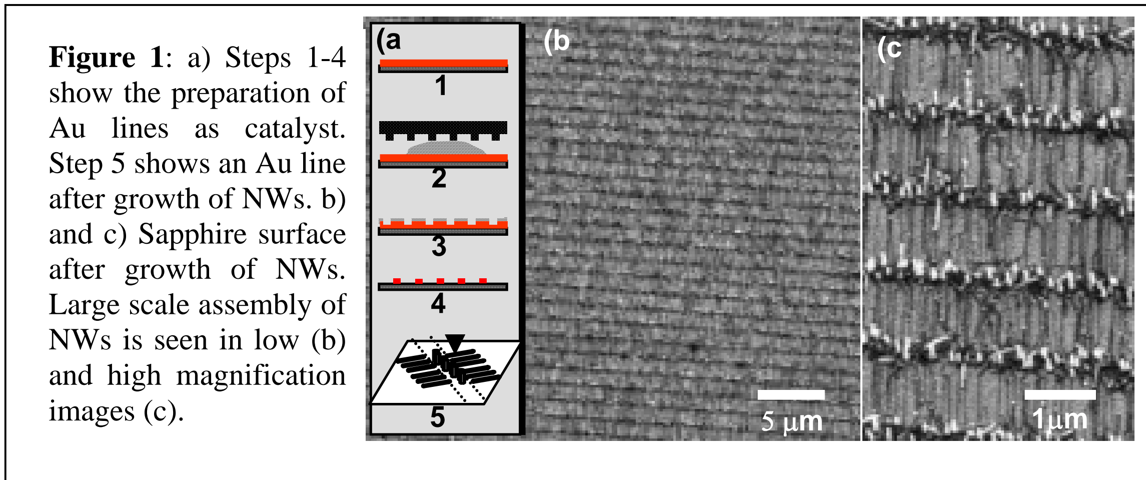


Figure 1: a) Steps 1-4 show the preparation of Au lines as catalyst. Step 5 shows an Au line after growth of NWs. b) and c) Sapphire surface after growth of NWs. Large scale assembly of NWs is seen in low (b) and high magnification images (c).

Future Plans: Our studies have focused on the growth and manipulation of semiconductor ZnO nanowires. These methodologies are now being implemented in the fabrication of heterostructured (ZnO/GaN) NWs for use as nano-emitting sources (laser diodes) and nano-detectors (photodiodes) with emphasis on optical properties and performance suited for applications in sensing and spectrochemical analysis.

Impact: This methodology will provide an inexpensive and straightforward approach to the synthesis of semiconducting, nanodevices (emitters and detectors) with multiple functionalities that can be integrated to form state-of-the-art measurement systems

Publication: B. Nikoobakht, C.A. Michaels, S.J. Stranick and M.D. Vaudin, **"**Horizontal Growth and *in situ* Assembly of Oriented Zinc Oxide Nanowires", Appl. Phys. Lett. **85**, 3244 (2004).

Title: Nanofabrication of Test Architectures for Molecular Electronics Applications

Authors: J. D Batteas (837), J.C. Garno (837) and C.A. Zangmeister (836)

Context: The ability to precisely construct nanoscopic metal-molecule-metal junctions is of great importance for the development of robust molecule based electronic and optoelectronic devices. By combining scanned probe lithography with electroless metal deposition, metal-molecule-metal junctions can be constructed where the dimensions and surface organization are dictated by the placement of surface groups active for electroless deposition, such as carboxylates, into a desired pattern. These structures will provide a means of measuring reproducibly transport (current-voltage) properties of ensembles of molecules with a fixed areal density to assess the role of the molecule in the transport process and to determine the scalability of per molecule conduction in such junctions.
Our objectives are to develop methodologies to construct confined molecular assemblies of metal-molecule-metal junctions with nanoscale dimensions for the evaluation of electron transport in small ensembles of molecules (10's – 1000's) to determine the scalability of per molecule conduction values in prototypical device architectures. To this end, automated scanned probe lithography is employed to pattern surfaces with self-assembled monolayers, where specific molecular linking groups are placed into organized structures on Au surfaces with features sizes ranging from ~ 10 nm – 200 nm in lateral dimension with the Au surface functioning as a bottom electrode. A completed metal-molecule-metal junction is then formed by the electroless deposition of metal yielding the top electrode. Here we have developed and demonstrated the needed fabrication capabilities to enable construction of these test architectures.

Major Accomplishments: Patterning of metal-molecule-metal junctions with nanoscale dimensions, specifically Cu on carboxylic acid terminated SAMs on Au, has been carried out using a combination of automated scanned probe nanofabrication and electroless metal deposition. The architecture of the nanostructures formed can be precisely tuned in all dimensions by controlling the lateral 2-D pattern size of the fabricated structures, the surface density of reactive acid groups placed into the structure, and the concentration of reactants in the electroless metal plating solution. An overview of the key steps to fabricate the Cu nanocontacts is illustrated in Figure 1. Using this approach metal structures ranging from ~ 20 nm to 200 nm in lateral dimension with 5 nm to 10 nm metal top contacts have been formed. An array of final structures fabricated using this approach is shown in Figure 2. The patterning process requires only on the order of 30 min for forming all of the

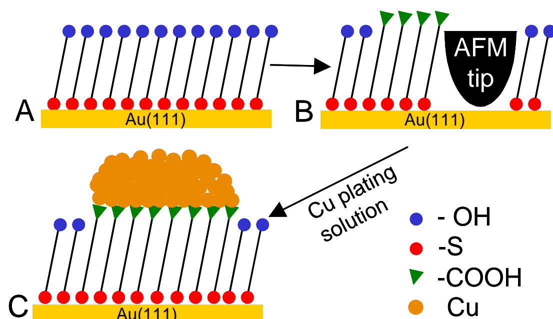


Figure 1. Scheme for fabrication of nanoscale metal junctions. (A) First a resist layer is deposited on the surface. (B) A structure of 16-MHA is then patterned into the resist by nanografting. (C) The surface is then exposed to a Cu plating solution yielding Cu deposition on the patterned acid layer.

junctions. This provides a means a fabricating a range of structures with varying dimensions to assess scalability of current with junction dimension and molecular packing density. This approach should be readily extended to other metals that can be electrolessly deposited such as Pt, and be applicable to the construction of more complicated multidimensional metallic structures including combined vertical and lateral junction geometries. Additionally, well-defined nanoscale metal-metal junctions can be also formed which may be employed in the development of enhanced optical spectroscopic methods for sensing.

Future Plans: Ongoing experiments are now aimed at probing the electrical behavior of ensembles of molecules within the nanopatterned junctions. These measurements can then be compared to those from prototypical device structures. This approach for building nanopatterned metallic structures will also be transferred to Si substrates as a means to construct hybrid semiconductor-molecule-metal junctions.

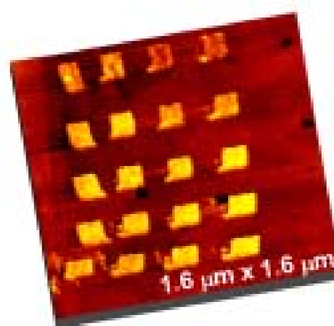


Figure 2. Topographic AFM image of nanopatterned array of sixteen 150 nm x 150 nm Cu structures (~ 5 nm high) on carboxylic acid terminated SAMs.

Impact: As academic, government and industrial laboratories pursue the development of nanoscale molecular based electronic devices, the approach described herein addresses the need for a robust systematic nanoscale test structure to critically evaluate electrical properties of candidate materials.

Title: Rapid searching of spectrum image databases for rare events, or finding the needle in the haystack when you don't even know you're looking for a needle!

Author: David S. Bright and Dale E. Newbury

Abstract:
We have developed the Maximum Pixel Spectrum, a software tool that enables rapid searching of SEM x-ray spectrum image databases to detect rare features, even if the analyst does not know in advance which elements are present. Single pixel features can be efficiently recognized and highlighted. Applications include contamination identification and localization and analysis of minority/trace phases.

Purpose: Characterization of the microstructure of materials often requires detection of rare features, such as naturally occurring minority/trace phases or unintentional particulate contamination. X-ray mapping in the SEM, a traditional tool for measuring elemental distributions with micrometer to nanometer spatial resolution, has recently been greatly enhanced by the development of x-ray spectrum imaging, in which a complete x-ray spectrum is stored at each pixel location visited by the beam. The silicon drift detector (SDD), described here in FY03 and whose development was aided by NIST SBIR grants, combined with digital signal processing enables x-ray count rates above 100 kHz, permitting recording of useful x-ray spectrum images in 200 s or less. The resulting stream of 200 Mbyte image databases is creating a demand for software tools that are quick and efficient at locating features of interest.

Major Accomplishments: We have developed a software tool within the NIST LISPIX image processing platform (available free at http://www.nist.gov/lispix/) that determines the MAXIMUM PIXEL SPECTRUM by finding the maximum value within each energy channel x-y plane and plotting this value versus energy. This new function is compared with the SUM SPECTRUM, similarly calculated by adding all values within a plane, as shown in Figure 1(a) for a spectrum image of Raney nickel, a methanation catalyst. Peaks in the SUM SPECTRUM correspond to common features in the x-ray spectrum image, as illustrated in Figure 1(b) where the aluminum-rich phases are highlighted.. While these same peaks are found in the MAXIMUM PIXEL SPECTRUM, additional peaks can be recognized that correspond to rare events, down to the single pixel level, shown in Figure 1(c) for a chromium contaminant that appears at a single pixel, or 1/51200 for a 256x200 scan. Note that the rare chromium feature has been found despite being completely unknown to the analyst.

Impact: The MAXIMUM PIXEL SPECTRUM has had an immediate impact in the microanalysis field. First publicly presented at the SCANNING 04 conference held in Washington in April, 2004, the method was immediately adopted by a U.S. manufacturer of microanalysis software systems, appearing in this vendor's system at the Microscopy and Microanalysis Conference in August and in their advertisement in Microscopy Today in September, 2004 (page 27). Other vendors are rapidly incorporating the MAXIMUM PIXEL SPECTRUM as a feature in their spectrum imaging software. We anticipate that the combination of SEM SDD x-ray spectrum imaging and derived spectrum image

processing tools will have a broad impact in materials analysis, supporting technology, physical and biological science, and forensic applications.

Future Plans:
The MAXIMUM PIXEL SPECTRUM and the SUM SPECTRUM are members of a class of transformations known as "derived spectra" to distinguish them from the true spectra recorded in the spectrum image. We plan to investigate additional algorithms for derived spectra to seek software tools that can aid the analyst in other aspects of x-ray spectrum imaging. Other microanalysis spectroscopies, such as electron energy loss and Auger electron, may also benefit from derived spectrum tools.

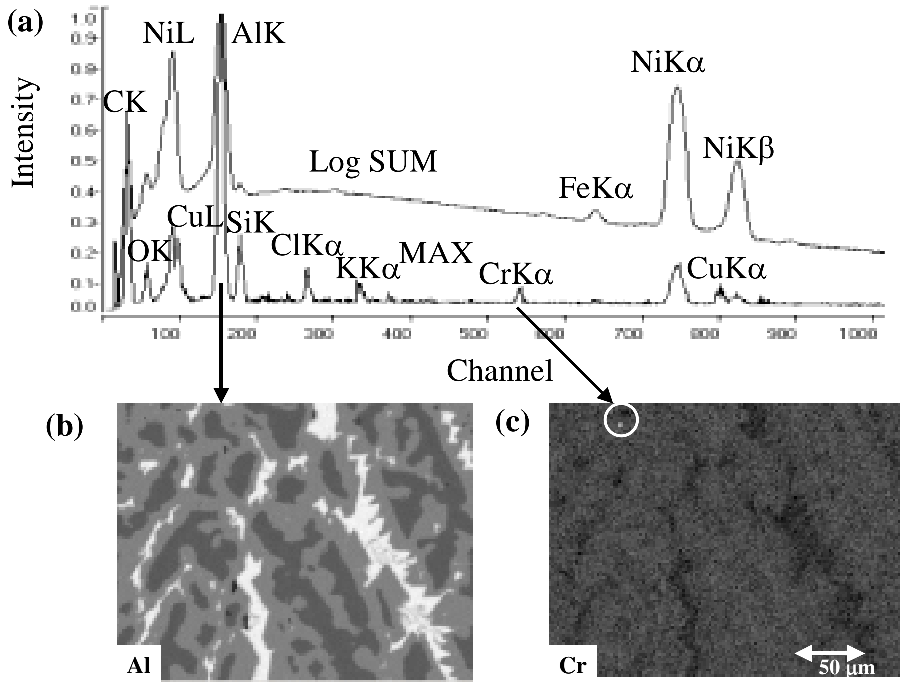


Figure 1: (a) SUM SPECTRUM (upper trace, log intensity) and MAXIMUM PIXEL SPECTRUM (lower trace, linear intensity). (b) A major feature (aluminum-containing areas recognized from peaks in the SUM. (c) A rare feature, chromium, detected at a single pixel (inside circle) from the MAXIMUM PIXEL SPECTRUM.

Title: Production of Uniform Particle Standards Using the Vibrating Orifice Particle Generator and Quantification by Optical Particle Sensor

Authors: Robert Fletcher, George Klouda and Greg Gillen (Div 837.05)

Vision: Currently there are no standard test materials for calibrating trace explosive detection devices like Ion Mobility Spectrometers (IMSs) for Homeland Defense and there is also a need for test particles to support basic research in particle removal from surfaces using air jets and swipe technologies. The Vibrating Orifice Aerosol Generator (VOAG) can produce monodisperse particles from 0.5 μm to 50 μm made from solution. Each particle contains the same amount of desired test compound which can be controlled by the solute concentration in solution. The precision and accuracy of the VOAG was determined at NIST to be approximately 1% using aerosol sedimentation (velocimetry) – heterodyne elastic light scattering experiments. The VOAG allows a wide range of compounds to be made into uniform particles. This is accomplished by dissolving the solute material in the appropriate solvent and delivering the solution by constant pressure through the 20 μm orifice that vibrates at 10kHz-100kHz (driven by a piezoelectric crystal). The number of particles made per second is the same as the driving frequency. The particle stream is dispersed by turbulent clean air flow and then subsequently dried in aerosol form in clean dry air. These dry, uniform particles of known composition are collected on a substrate such as a filter or impacted onto a plate or surface. One complication is that although the number of particles made is known and related directly to the crystal oscillation frequency, the number delivered to the substrate can be greatly diminished due to particle loss during transport from generator to substrate.

An important addition to the VOAG for generation of standard particles would be a capability to accurately quantify the number of particles delivered to the substrate. The detection method must be on-line, non-intrusive and non-destructive. One approach would be to use an in-line optical particle sensor (an individual particle extinction sensor) that would count each particle that passes through the sensor region and that is subsequently collected on the substrate. An additional benefit of this approach is that an extinction sensor can provide particle size and particle uniformity information in a rapid manner.

Purpose: The purpose of this effort is to develop a method to produce accurate and precise particle standards of known composition, size and number for testing IMS instruments, trace analysis, particle testing and for pharmaceutical research. The VOAG produces highly precise particles and the optical particle counter will quantify the number and thus the amount of test compound.

Major Accomplishments: The operating characteristics and verification of precise particle-making capabilities using a Vibrating Orifice Aerosol Generator (VOAG) has been demonstrated. For trace explosive research, we have used the VOAG to produce 8μm fluorescein particles containing a trace amount of RDX (weight % RDX $= 6.7\text{x}10^{-5}$ %) as shown in Figure 1. The particles appear agglomerated due to the heavy loading on the filter but were single particles as an aerosol. These particle-filter collections were

examined by a commercial trace explosives detector based on IMS and gave a positive alarm for RDX.

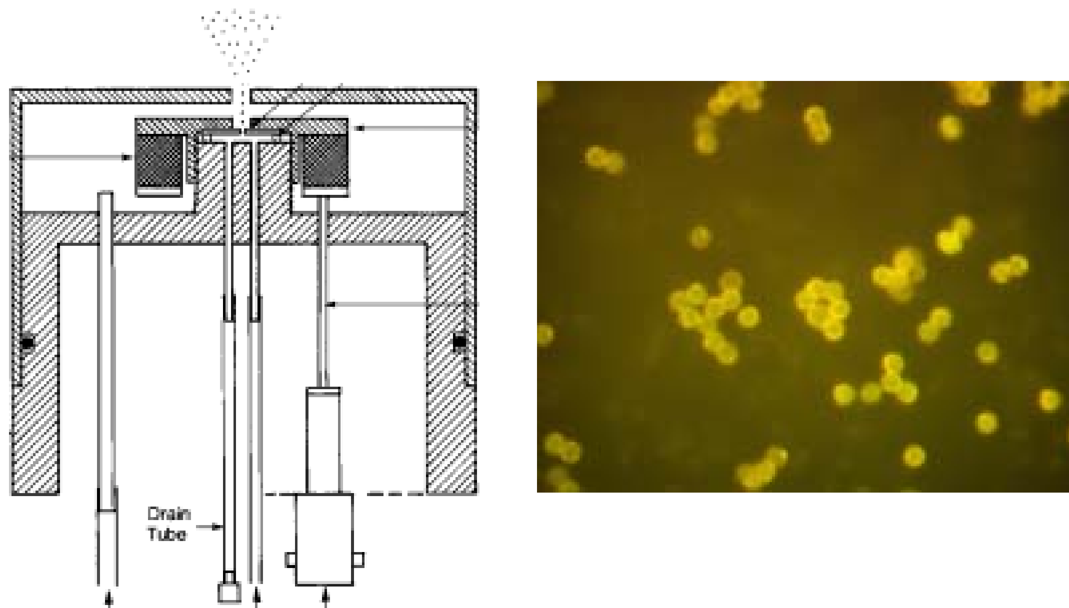


Figure 1. Schematic of the VOAG and a fluorescence optical micrograph of fluorescein-RDX particles produced by the VOAG.

Impact: The ability to make trace particle standard test materials in a custom fashion for many materials is a valuable addition to our capabilities. Instruments that detect trace explosives and trace drug quantities can be tested and their performance quantified.

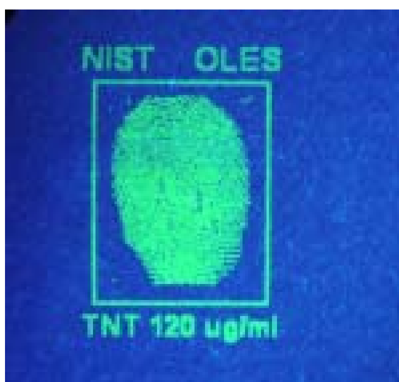
Future Plans: We are developing an in-situ particle counter that will be used in-line to detect monodisperse particles as they are being deposited on the substrate. Several experts in optical particle sensor design have been contacted and a system has been designed and will be fabricated in FY2005. The detector, which will be based on an extinction or light scattering sensor, will permit not only counting of the deposited particles but also a measure of particle size and uniformity. Also, we hope to extend the capabilities of the VOAG to produce custom biodegradable polymer spheres containing known amounts of pharmaceuticals to support a growing program in microanalysis of biomaterials and drug delivery systems.

Title: Advanced InkJet Printing Technology for Trace Explosives Standards

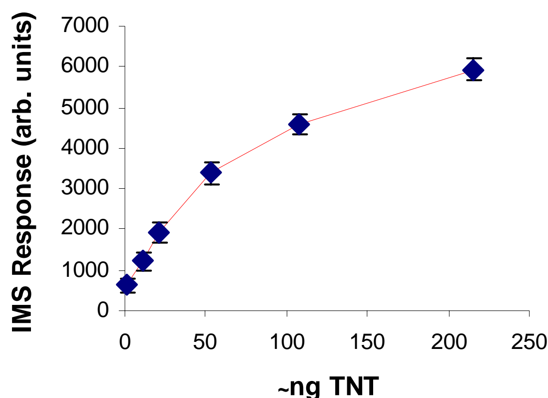
Authors: Greg Gillen , Robert Fletcher, Jenny Verkouteren, Mike Verkouteren and George Klouda, Div 837, CSTL

Vision: Current national priorities in homeland security have led to an unprecedented level of utilization of trace explosive detection systems for counter terrorism and law enforcement. A critical and immediate need is to develop a chemical metrology and standards infrastructure to support the widespread operational deployment of tabletop, handheld and portal- based trace explosive detection systems now being used in airports, military installations and in law enforcement applications.

Purpose: The purpose of this effort is to develop prototype standard reference materials for calibration and optimization of trace explosive detection instruments. We are exploring drop-on-demand inkjet printing as a low cost, flexible and reproducible method for preparation of explosive standards over a wide range of concentrations on almost any substrate.



Inkjet printed fingerprint containing TNT and



IMS response curve for TNT standard inkjet printed directly on

Major accomplishments: A new piezoelectric inkjet printer system at NIST has been used to prepare prototype explosive standard reference materials on a variety of substrates. Inkjet printing potentially offers a flexible, rapid and reproducible method for preparation of explosive standards. Using a single standard solution, a large range (10^6) in deposited quantity of explosive can be achieved by changing the number of drops delivered to the sample without the need for serial dilutions. Using four printheads allows mixtures of virtually any composition to be prepared. The NIST printer system has been used to prepare prototype calibration standards by drop-on-demand printing of RDX, PETN and TNT from isobutanol solutions onto various substrates. The concentration of explosives delivered in individual inkjet droplets is determined by GC-MS analysis or by determination of droplet diameter using digital camera imaging with high frequency strobe illumination. A second sample type involves printing of digitized human fingerprints using RDX or TNT as the printing media. To visualize the location of the fingerprint, a fluorescent dye is co-jetted with the explosives.

Future Work:

We are working to improve the quantitative delivery of solution using inkjet printing. The NIST printer system is being modified to use optical particle counting for real-time evaluation of the number of drops ejected and the individual droplet size. The next phase of the project will be to print explosives containing polymers to more accurately simulate actual high explosive materials.

Title: Detection of Trace Anthropogenic Contamination in Aquatic Ecosystems using Fluorescence Excitation-Emission Matrix Spectroscopy

Authors: R. David Holbrook and Paul C. DeRose (839)

Purpose: Aquatic resources play a key role in supporting and maintaining human activity. Aquatic systems provide potable water supplies to meet growing drinking and agricultural water requirements, and are used as receiving streams in the disposal of treated wastewater effluent. However, the nearly ubiquitous presence of trace organic contaminants in receiving streams [1] has prompted worldwide concern about their impact on human health, largely due to the documented sexual disruption of aquatic wildlife caused by some trace contaminants [2]. Current analytical procedures for measuring trace organic contaminants in aqueous samples are both expensive and laborious, indicating the need for a sensitive screening method that is capable of detecting organic compounds that originate from biological wastewater treatment systems.

This investigation was undertaken to determine whether fluorescence excitation-emission matrix spectroscopy, or EEM, is an applicable means of distinguishing treated wastewater effluent from "uncontaminated" receiving water samples.

Context: The high frequency of contaminant detection in aquatic systems and extremely low biologically-active concentration (i.e., ng/L) recently led the National Research Council to recommend better monitoring of receiving streams [3]. A simplified screening method would facilitate a wider range of samples/environments being examined. It is expected that environmental practitioners would be the immediate beneficiaries, followed by the general public if a link between these compounds and human health is established.

Major Accomplishments: A method of EEM collection and data analysis was developed using samples collected upstream and downstream of an advanced wastewater treatment facility. The EEM procedure took approximately 20 minutes per sample, required little sample volume (< 10 mL) and few preparation requirements. Data analysis was adopted from Chen et al. [4]. A unique fluorescence distribution was observed for the downstream samples (Figure 1), indicating that the presence of treated effluent could be detected using EEM. Specifically, a significant increase in fluorescence intensity was observed in region 1 (aromatic proteins) at excitation wavelength between 230 nm and 260 nm and emission wavelength between 300 nm and 340 nm (Table 1). The signature fluorescence distribution of downstream samples is noteworthy due to the extensive treatment processes employed at this facility. The fluorescence distribution of treated effluent derived from less advanced technology is even more unique (data not shown).

Impact: The EEM collection and analysis technique provides a quick and cost-effective means of screening aqueous samples for possible anthropogenic contamination. This method will provide a qualitative tool for allocation of sampling and analytical resources.

Future Plans: It is expected that a similar technique may be adopted for Homeland Security needs involved in protected potable water supplies.

Literature Cited

1. Kolpin, D.W.; Fuling, E.T.; Meyer, M.T.; Thurman, E.M.; Zaugg, S.D.; Barber, L.B.; Buxton, H.T. *Environ. Sci. Technol.* **2002,** 36, 1202-1211.
2. Thorpe, K.L.; R.I. Cummings; T.H. Hutchinson; M. Scholze; G. Brightly; J.P. Sumpter; C.R. Tyler. *Environ. Sci. Technol.* **2003,** 37, 1142-1149.
3. National Research Council, *Hormonally Active Agents in the Environment*. National Academy of Sciences, USA, (1999).
4. Chen, W.; Westerhoff, P.; Leenheer, J.A.; Booksh, K. *Environ. Sci. Technol.* **2003,** 37, 5701-5710.

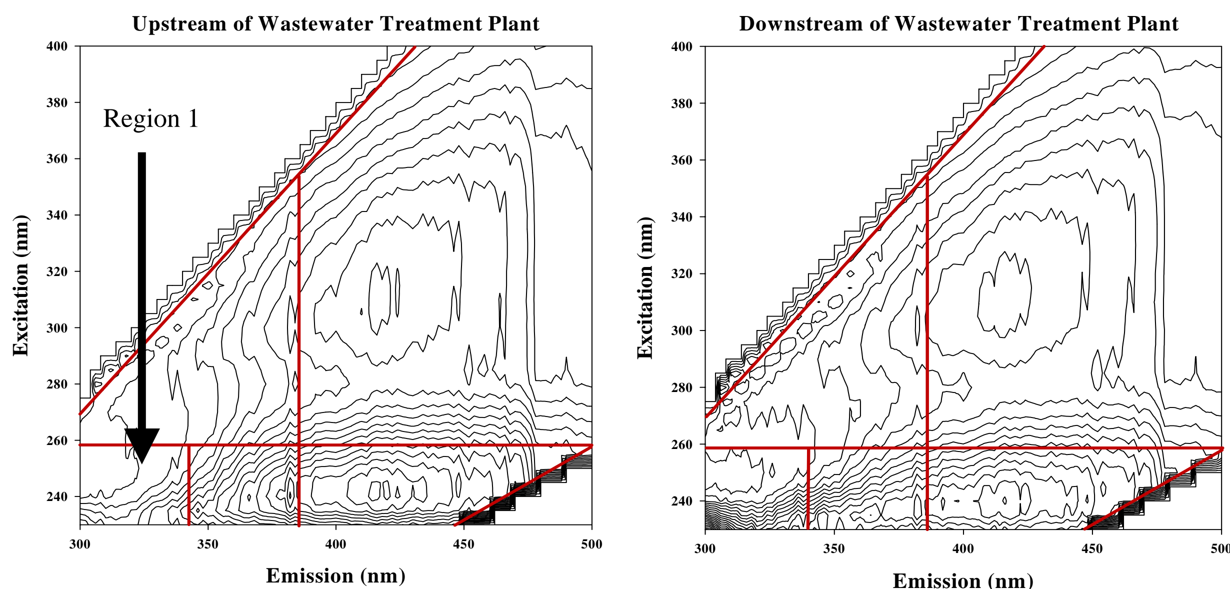


Figure 1. Typical EES contour plots of upstream (left) and downstream (right) samples. The red lines are the superimposed regions that are described by Table 1. Note the increase in fluorescence intensity in Region I (lower left area) between the upstream and downstream samples. Each contour line represents 1/20th of the maximum fluorescence intensity.

Table 1: Excitation-Emission Region Description and Results of Regional Integration of Upstream and Downstream Samples.

	Organic Matter Type	Excitation Wavelength (nm)	Emission Wavelength (nm)	Portion of Total Fluorescence Signal (%) Upstream (n = 6)	Downstream (n = 15)
Region I	Aromatic Proteins	230 to 260	300 to 340	9.9 ± 0.3	13.5 ± 2.3
Region II	Aromatic Proteins	230 to 260	340 to 380	25.5 ± 0.8	26.3 ± 1.3
Region III	Fulvic Acids	230 to 260	380 to 500	42.5 ± 0.5	38.7 ± 3.1
Region IV	Soluble Microbial Products	260 to 400	300 to 380	8.8 ± 0.1	9.4 ± 0.6
Region V	Humic Acids	260 to 400	380 to 500	13.3 ± 0.4	11.9 ± 0.9

Results are average ± standard deviation.

Title: Improved Energy Stability in the NIST Microcalorimeter X-ray Detector

Authors: Terrence Jach, John A. Small, Dale E. Newbury

Purpose: Microcalorimeter x-ray detectors make up a new technology that combines some of the positive features of wavelength dispersive (high resolution) and energy dispersive (parallel detection over a wide energy range) detectors that have gained broad acceptance in the microanalysis community. Microcalorimeters which use a transition edge sensor (TES) have proven to be effective over energy ranges of 10 keV or more in application such as x-ray fluorescence analysis with electron microscopes. TES microcalorimeter x-ray detectors have successfully demonstrated energy resolutions better than 5 eV. However, serious drifts in energy scale over extended counting times have set limits on both the long-term resolution and the calibration of these detectors. This is because the operating point of the detectors is the middle of the superconducting-normal phase transition. The successful operation of a microcalorimeter as an x-ray detector puts considerable constraints on the stability of all the electrical and thermal inputs to the instrument. We investigated the sources of energy scale drift in the microcalorimeter x-ray detectors developed by NIST (Boulder) and have addressed the most critical elements. Previously observed drifts of >10 eV/h have been reduced to 1-2 eV/h. This improved stability, shown in Figure 1, has resulted in the observation of x-ray fluorescence linewidths of 12-15 eV over a 6 h time period.

Major Accomplishments: The detector is cooled to a substrate temperature of only 70 mK and maintained at its operating point by a complex feedback control system connected to a large superconducting magnet. We carried out a careful analysis of the performance of all the elements in the control system including the response function of the magnet under typical conditions of operation. We determined that the desired stability and performance of the detector required control of its substrate temperature to a precision of 23 μK, that is, a variation of less than 5 parts in 10,000. By careful modification of the control circuitry, we have been able to realize this degree temperature stability of the substrate. The energy scale of spectra is now observed to be stable to within about ≤1 eV/h over a period of hours, under operating conditions in which a linewidth of 12-15 eV is readily obtained. X-ray spectra acquired over long durations under these conditions of substrate temperature stabilization show vastly improved stability and resolution.

Impact: The drift in energy scale of the microcalorimeter x-ray detector has been a major limitation to the commercial development and marketing of this type of detector. There are currently a number of potential applications of this detector, particularly for microanalysis, which are eagerly awaited in the semiconductor industry. Semiconductor manufacturers have already indicated an interest in using this type of detector if the problems can be solved.

Future Plans: Additional measures to stabilize the operating temperature are possible. Once realized, we can carry out a demonstration of the microcalorimeter detector with an electron microscope for quantitative microanalysis. We also anticipate replacing the actual detector element with higher resolution (< 4 eV) versions which have been developed at NIST, Boulder. Combined with the achieved stability of the energy scale, we can start to look at characterizing chemical state of some elements by the energy of their fluorescence lines.

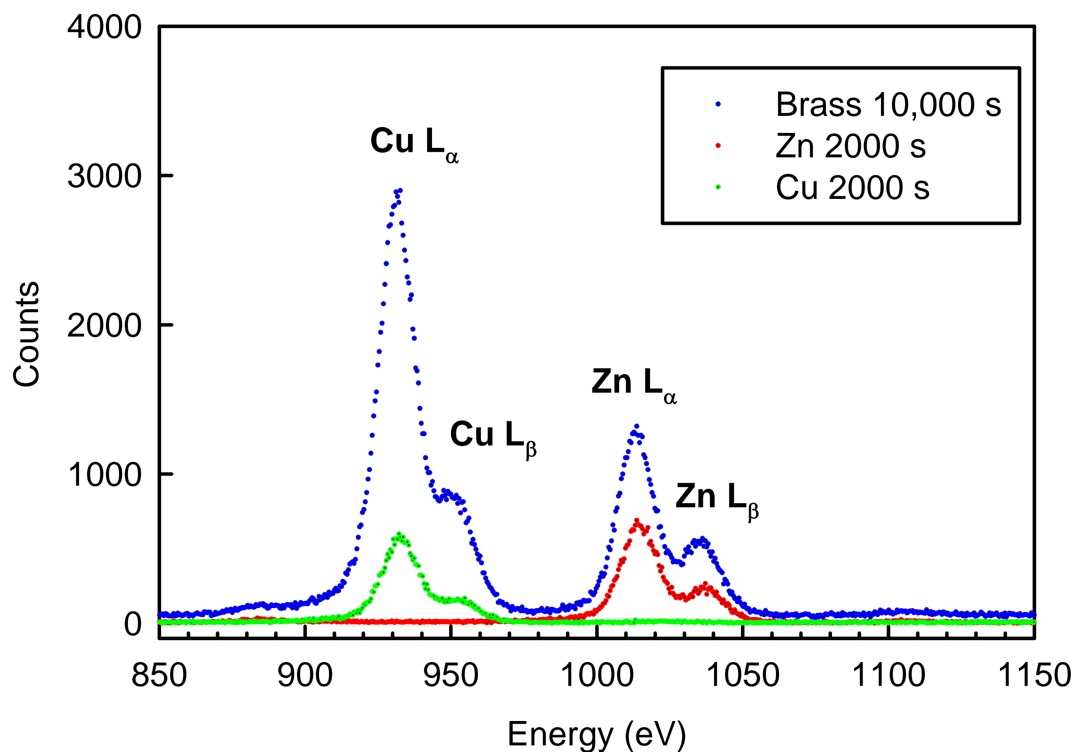


Figure 1, X-ray spectra collected on the NIST microcalorimeter detector after control circuit modifications. The spectra were collected for a total of 14,000 s live time over a 6 h time period.

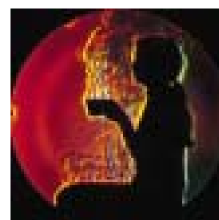
Title: Portal Filter Particle Collection Efficiency Using Mondispersed Aerosol

Authors: G.A. Klouda, R.A. Fletcher and G. Gillen (837)

NIST has established the capability to evaluate the performance of air filtration systems. Although general filter specifications are usually available from manufacturers, many filter manufacturers know less about the performance of their filters for aerosol of a particular size and composition. In a time of strong National Defense against terrorist attacks, an existing technology has emerged as one of the most effective means of detecting high-energy explosives and identifying potential perpetrators. Trace explosives detection systems are almost entirely based on ion mobility spectrometry (IMS) that rely on efficient microscopic-size particle sampling to concentrate trace explosives for subsequent desorption (heating) of these compounds into the IMS for detection.

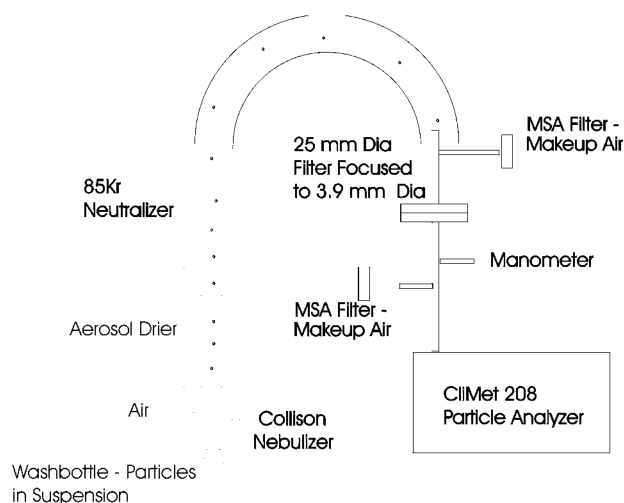
Air Jet Portal

Convective Airflow



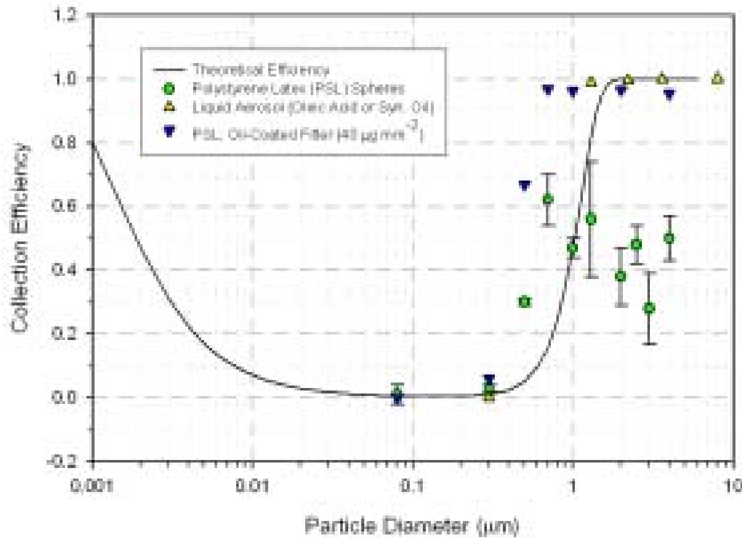
To meet the immediate need to screen people's clothing of trace explosives in a noninvasive way at airports and government facilities, two emerging portal technologies were designed to utilize air jetting and convective airflow to dislodge and transport microscopic particles from clothing to filters for desorption into an IMS system. However, no data existed on just how efficient these filters were at collecting particles of known size and composition. The NIST Analytical Microscopy Group, in collaboration with the NIST Office of Law Enforcement Standards, the Transportation Security Administration and the Department of Homeland Security, has characterized the collection efficiency of the metal-fiber filter material used by the manufacturers of these portal systems.

Filters were evaluated using airborne particles ranging in diameter from 0.08 µm to 8 µm at operational airflow velocities (10 m s^{-1}). The filter collection efficiency was measured by generating aerosol of known size using two standard methods, either a Collison Nebulizer for aerosolizing polystyrene latex (PSL) spheres or a vibrating orifice aerosol generator (VOAG) to produce sticky liquid oleic acid aerosol of known size. The dried and neutralized aerosol flows through a filter holder, with and without the filter in place, and into an optical particle analyzer to determine the particle concentration. The filter



Experimental setup for measuring portal filter particle collection efficiency.

efficiency is calculated from the concentration measured with and without the filter present. These results will likely lead to a better understanding of what size of explosive particles are collected, and consequently possible ways of improving the sampling and collection efficiencies.



Filter collection efficiency plotted vs. particle size for different type aerosol. PSL variability is due to particle bounce. Collection efficiency is greater when filter fibers are coated with oil or for sticky particles, *e.g.* oleic acid.

Future experiments will include the use of the VOAG to generate an aerosol of a high explosive and of a plastic binder, similar to a composite explosive, *e.g.* C4, for evaluating filter efficiency and for developing a standard test surface for IMS. NIST capability of generating and counting monodispersed aerosol can be applied to virtually any filtration system.

Title: Reference Material (RM) 8785 Air Particulate Matter on Filter Media

Authors: G.A. Klouda, J.J. Filliben (ITL) and H.J. Parish (SRI International)

Combustion aerosol has a major influence on air quality and is known to have a direct and indirect impact on the Earth's radiative forcing. For the most part, man's activities are linked to these emissions and account for a significant amount of the total carbon aerosol found in the atmosphere. To assess impacts and distinguish sources of combustion aerosol, numerous methods exist to quantify the amount of organic and black (soot) carbon, important in addressing air quality issues and estimating the warming and cooling effects of aerosol on our climate system. However, all these analytical methods are method dependent and result in various definitions of what constitutes black carbon.

SRI Dust Generation and Collection

Researchers in the Analytical Microscopy Group (CSTL) and the Statistical Modeling and Analysis Group (ITL) have collaborated with SRI International (Menlo Park, CA) to produce Reference Material (RM) 8785 Air Particulate Matter (PM) on Filter Media. RM 8785 was produced by resuspending SRM 1649a Urban Dust, sampling its' fine fraction (< 2.5 μm aerodynamic diameter) and filtering the $PM_{2.5}$ onto nearly 2000 quartz-fiber filters. Filter ID number and the gravimetrically determined mass of fine SRM 1649a uniquely identify each filter. RM 8785 is intended primarily for use in the evaluation of analytical methods used to characterize the carbon composition of atmospheric $PM_{2.5}$ for national ambient air quality standards (NAAQS) monitoring programs. Additionally, RM 8785 will provide the atmospheric chemistry and ocean-sciences community with a means to intercompare methods and laboratories for the measurement of black carbon.

Through an inter–laboratory and –method comparison involving NIST, Desert Research Institute (Reno, NV) and Sunset Laboratories Inc. (Tigard, OR), concentrations of total carbon, black carbon and organic carbon were measured and values were assigned. Measurements were performed using two widely used thermal-optical methods: the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the Speciation Trends Network-National Institute of Occupational Safety and Health (STN-NIOSH). RM 8785 has been assigned a reference value for total carbon concentration and information values for black and organic carbon concentrations corresponding to each method.

CONTACT: George Klouda (CSTL), ext. 3931; Jim Filliben (ITL), ext. 2855

Title: Cluster SIMS Depth Profiling in Polymeric Blends for Protein Drug Delivery Applications

Authors: Christine Mahoney[1], Peter Yu[2], and Joseph A. Gardella Jr.[2]

Affiliation: [1]National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8371, Gaithersburg, MD, 20899-8113, USA. [2]State University of New York at Buffalo, Chemistry Department, Buffalo, NY, 14260-3000

Vision: Metrology to monitor the in-depth composition in polymeric blends utilized for drug delivery and tissue engineering applications is essential for understanding biocompatibility and drug release issues. With the advent of cluster Secondary Ion Mass Spectrometry (SIMS), we are now able to obtain in-depth information from polymeric blends and potentially relate the sub-surface composition to the performance characteristics in real devices.

Purpose: Poly(L-lactic acid) (PLLA) has shown particular promise as a biodegradable material because the degradation product, lactic acid, is readily metabolised by the body. In addition, the degradation rate can be easily controlled through variation of its molecular weight. Polyethylene oxide (PEO)-containing copolymers, such as Pluronic® surfactants (containing polypropylene oxide (PPO) and PEO components) are also useful polymeric materials for biomaterial and pharmacological applications as they are neutral, highly biocompatible and pharmacologically inactive water-soluble polymers. The incorporation of PEO-containing copolymers into biodegradable PLLA-based drug delivery implant systems is expected to improve the interfacial biocompatibility of the polymeric devices as a result of the preferential migration of the PEO component to the surface. In addition, blend matrices of PEO and relatively hydrophobic PLLA is also expected to improve the three dimensional stability and the biological activity of water-soluble macromolecular drugs such as proteins or enzymes in the delivery systems via micelle formation. When used as drug-releasing matrices, these PLLA/Pluronic® blends have been proven to extend protein release and minimize the initial protein burst when compared to the pure PLLA homopolymers. The composition in the sub-surface region (10-1000 nm) of these materials is highly important as it will determine the extent of initial burst release of any drugs present as well as the biocompatibility of the material. Until now, no methodology has been capable of yielding in-depth information from this region.

Scientific and Technical Research and Development: The surface chemistry as determined by both X-ray Photoelectron Spectroscopy (XPS) and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) of these PLLA/Pluronic® blend materials indicates that there is an enrichment of the Pluronic® at the surface. However, these initial surface studies utilized monatomic primary ion beams, which cause significant subsurface damage particularly in organic and polymer samples. This increased beam induced damage prevents the ability to obtain information as a function of depth in organic and polymer samples. Compared to conventional SIMS, "cluster SIMS" employing molecular rather than atomic primary ion beams, often yields enhanced sensitivities, decreased accumulation of beam-induced damage, and increased sputter rates. These advantages

have allowed us to obtain in-depth information from certain organic and polymeric materials for the first time.

Major Accomplishments: Figure 1 shows the resulting in-depth profiles obtained from a PLLA/Pluronic blend system containing 25% (w/w) Pluronic®. This depth profile represents our first successful attempt to obtain in-depth information from polymeric blend systems using SIMS. These profiles are consistent with a surface enrichment of Pluronic®-P104 surfactant, followed by a depletion zone, and then finally a constant bulk composition region. This effect was consistent over a range of concentrations (1-25%). Because of the well-behaved nature of these materials under cluster ion bombardment, we have also successfully obtained quantitative depth profiles (figure 1b). These results demonstrate that with cluster primary ion bombardment, we are now able to successfully monitor and quantify the preferential segregation that occurs within certain multi-component polymer blends.

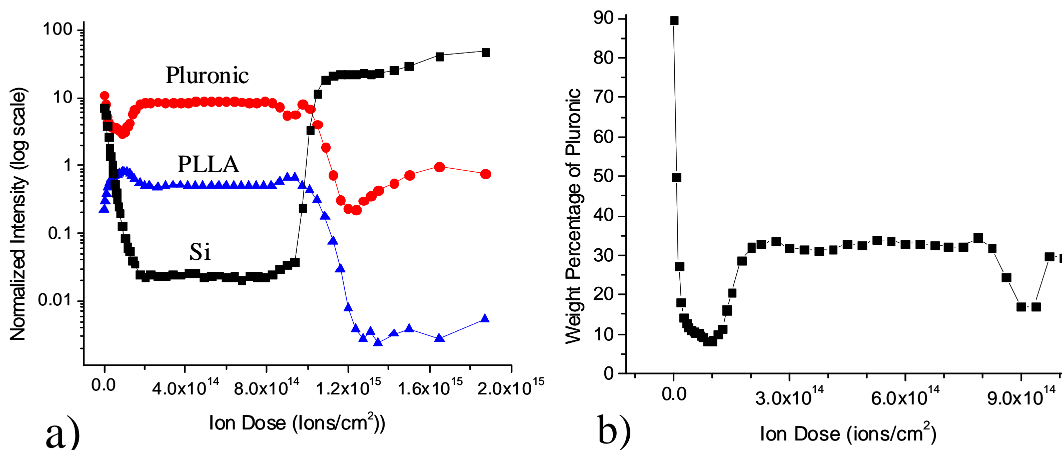


Figure 1: Cluster SIMS depth profiles of 25% (w/w) Pluronic® surfactant in poly(L-lactic acid) (PLLA) spin cast onto silicon (~620 nm). a) Normalized signal intensities associated with Pluronic® (m/z = 59), PLLA (m/z = 128) and Si (m/z = 28), plotted as a function of increasing SF_5^+ primary ion dose (increasing depth), and b) Composition depth profile of Pluronic in PLLA using SIMS calibration.

Impact: The development of cluster Secondary Ion Mass Spectrometry (SIMS) for in-depth analysis of polymeric biomaterials has potential long-term impact for quality control and product development in the biomedical/pharmaceutical arenas.

Future Plans: In the future, we plan to determine the 3-D molecular structure of these and other drug delivery systems (such as drug eluting stents and insulin delivery systems). We plan to monitor the diffusion and release of proteins and drugs from these systems using cluster SIMS technology. In addition to this, collaborations are being established with pharmaceutical and biomedical device manufacturing industries in order to relate the 3-D compositional structure to the performance characteristics in real devices.

Title: Chemical Characterization of SiGe Single Crystal Specimens and SiGe Films on Silicon with Electron Probe Microanalysis

Authors: R. B. Marinenko, D. Klinedinst, L. Richter, D. Simons, S. Turner, J. A. Small, E. Steel, and F. Stevie (North Carolina State University)

Purpose: Develop Reference Materials consisting of SiGe on Si for semiconductor analysis laboratories to use for in the characterization of SiGe thin-film components.

Major Accomplishments: We investigated three aspects of the SiGe thin-film project in an effort to prepare Reference Materials of SiGe on Si for. First, thin films of SiGe on 8-inch diameter Si wafers prepared by Agere Systems were studied for heterogeneity with wavelength dispersive electron probe microanalysis (WD-EPMA). Twelve specimens cut into 2 cm x 2 cm sizes from 2 different wafers were assessed. The nominal compositions of the two films studied are 0.0384 and 0.341 mass fraction Ge, and the approximate thickness of the films were 95 nm and 170 nm, respectively. Specimen to specimen heterogeneity was anticipated since a circular halo-like region thicker than for the rest of the disk was observed around the disk center by Secondary mass spectrometry (SIMS) and elipsometry. Therefore specimens selected for testing were taken from a region of the wafer where the specimen-to-specimen thickness variation was expected to be minimal. Using a point beam, with repeated readings on 10 points per specimen the extent of heterogeneity within each specimen (point to point) and between specimens as well as the experimental uncertainty were assessed. The expanded uncertainty, including all heterogeneity contributions, was determined to be 2.0-2.5% relative or less for Ge in 10 specimens.

Second, a heterogeneity assessment was conducted with WD-EPMA of five specimens cut from each of the of the SiGe14 and SiGe6.5 standard boules that had been previously assessed for heterogeneity in 2003. The Ge in these five specimens had been analyzed with INAA and a sixth specimen had been analyzed by ICP-OES. We determined that the same sample to sample trends in the Ge composition by INAA were observed by WD-EPMA. Data, including backgrounds, were acquired at three different excitation potentials to also enable quantification and evaluation of matrix correction procedures. This evaluation is ongoing at this time with the intention of comparing results with INAA and ICP-OES.

Third, new thicker SiGe films on Si were prepared for NIST by Advanced Semiconductor Materials. Since these films are approximately 4 μm thick, it will be possible to treat them as bulk specimens with regards to quantitative electron microprobe analysis. Four specimens cut from two different disks with nominal compositions of SiGe10 and SiGe25 have been tested using traverses and duplicate readings on random points to assess the heterogeneity. In addition, data was acquired at three excitation potentials with background readings for quantification. Data from all traverses including within and between specimen heterogeneity show that the expanded uncertainty (k=3, 99%) is less than 1% relative for both Si and Ge and is only slightly greater than the counting statistics error predicted from Poisson statistics. Evaluation of the random point heterogeneity data and quantification procedures is in process.

Impact: This work will provide the semiconductor industry with a reference material it needs for the evaluation of SiGe components.

Future Plans: Data from the standard boules will be used in conjunction with Monte Carlo calculations to determine the optimum voltage and corrections procedures for microprobe analysis of the thicker films. Once the data analysis is completed, the materials will be released for distribution as Interactive Materials during the first half of FY05. We will also continue to evaluate procedures for the quantitative electron probe analysis of the thinner films discussed in the first part of these studies.

Title: Effects of Backscattered Electrons on the Analysis Area in Scanning Auger Microscopy

Authors: *Cedric J. Powell; Aleksander Jablonski (Institute of Physical Chemistry, Warsaw, Poland)*

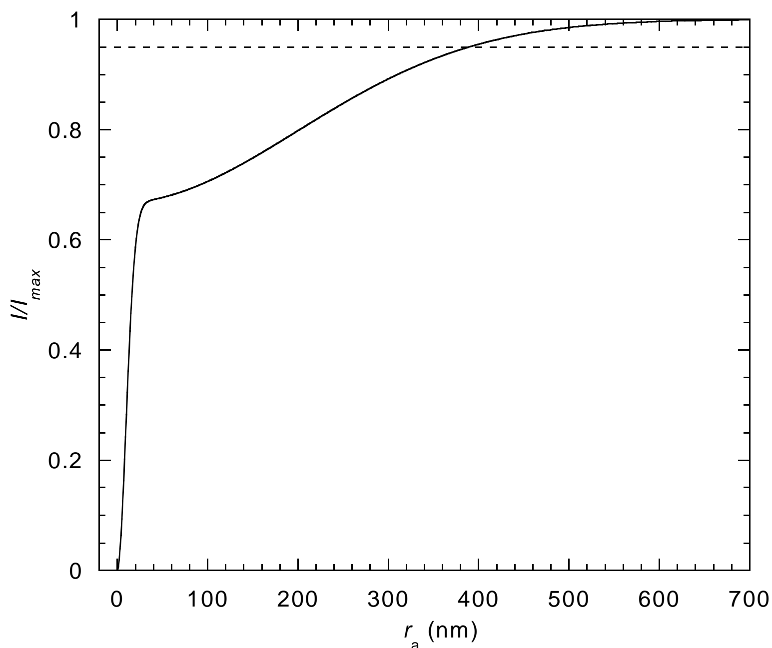
Vision: To provide reference data, models, and reference procedures to enhance the accuracy and efficiency of surface analyses made by Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), thereby improving the traceability of chemical measurements.

Purpose: To evaluate the effects of backscattered electrons on the analysis area in scanning Auger microscopy.

Context: AES is a commonly used technique of surface analysis. For example, it is used in the semiconductor industry to identify unwanted particulates and other defects on wafer surfaces that are detected after various processing steps. In this and similar applications, a focused electron beam (with a width of about 10 nm) is directed onto the feature of interest, and a measurement made of the surface composition. Analysts typically assume that the detected Auger-electron signal originates from an area defined by the width of the incident beam. The analysis area, however, is generally much larger due to the detection of Auger electrons resulting from inner-shell ionizations induced by multiply scattered primary electrons in the vicinity of the sample surface (i.e., by so-called backscattered electrons).

Major Accomplishments in FY2004: This work proceeded in two phases. First, a simple analytical model was used to estimate the effects of backscattered electrons on the analysis area in scanning Auger microscopy (SAM). For normally incident electrons, the radius r_a of the analysis area was calculated corresponding to detection of 80 %, 90 %, and 95 % of the total Auger-electron signal as a function of two sample parameters, the backscattering factor R and a Gaussian parameter σ_b describing the radial distribution of backscattered electrons. For a reasonable range of these parameters, r_a depended linearly on σ_b and to a lesser extent on R. Values of r_a can be appreciably larger, by up to a factor of 100, than the typical widths of the incident beam in modern SAM instruments.

As an example, the Figure shows the ratio of the Auger signal within an area of radius r_a to the maximum Auger signal (for an infinite radius) for an illustrative case in which σ_b = 200 nm and R = 1.5 (typical values for a primary beam energy of 20 keV). In this example, two-thirds of the total Auger signal originated from ionizations by the primary beam and was emitted from an area of radius 30 nm. The remaining one-third of the total signal originated from ionizations by backscattered electrons and was emitted from a much larger area, with 90% from an area of radius about 310 nm, 95 % from an area of radius about 390 nm, and 99 % from an area of radius about 530 nm. The parameter σ_b can be up to about 1 μm for some materials at a primary energy of 20 keV, and r_a can then be up to about 2 μm (for detection of 95 % of the total Auger intensity).



Plot of I/I_{max}, the ratio of the Auger intensity from a circular area of radius r_a to the total Auger intensity from a circular area of infinite radius, as a function of r_a.

In a second phase of the work, Monte Carlo simulations were made to investigate the radial distributions of Auger electrons from a thin copper film on substrates of silicon and gold for normally incident primary electrons with energies of 5 keV and 10 keV. These simulations confirmed the general trends found in the first phase. Values of r_a (for detection of 95 % of the total Auger intensity) ranged from 30 nm (Au substrate, primary energy of 5 keV) to 680 nm (Si substrate, primary energy of 10 keV).

Impact: Most "point" analyses by AES have been previously based on the implicit assumption that the entire detected signal originated from the feature of interest. When Auger analyses are required of fine particles on surfaces or of inclusions in matrices, it will generally be necessary to reduce the beam energy to ensure that most of the signal comes from the feature rather than from regions far from the feature. As a result, a tradeoff may have to be made between spatial resolution, analytical sensitivity, and validity of the analysis.

Future Plans: A new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) of multilayered thin films by AES and XPS will be released in FY2005. It is hoped to extend the capabilities of this database in the future to allow simulations of AES spectra for fine particles on surfaces and inclusions within samples.

Publications: C. J. Powell, "Effect of Backscattered Electrons on the Analysis Area in Scanning Auger Microscopy," Appl. Surf. Science 230, 327 (2004); A. Jablonski and C. J. Powell, Monte Carlo Simulations of Electron Transport in Solids: Applications to Electron Backscattering from Surfaces," Appl. Surf. Science (in press).

Title: Optical Characterization of Organic Electronic Thin Films

Authors: L.J. Richter (837), M.C. Gurau (837), D.M. DeLongchamp (MSEL)

Context: Organic electronic (OE) devices are projected to revolutionize integrated circuits through new applications that take advantage of low-cost, high volume manufacturing, nontraditional substrates, and designed functionality. OE devices, which rely on custom designed organic molecules and polymers instead of crystalline inorganic material such as silicon, present the electronics industry with fundamentally different measurement challenges. For example, the structural order in ultrathin OE films, particularly at the buried film/gate-dielectric interface, is thought to be critical to the achievement of high performance. However, x-ray diffraction techniques, the 'gold standard' for structural determination, are difficult with very thin films. Additionally, as many target applications require flexibility in the OE film, true crystalline order (which gives rise to diffraction) may be undesirable. In this exploratory research project, optical techniques originally developed for the characterization of molecules adsorbed at surfaces are explored as tools for the structural characterization of thin films.

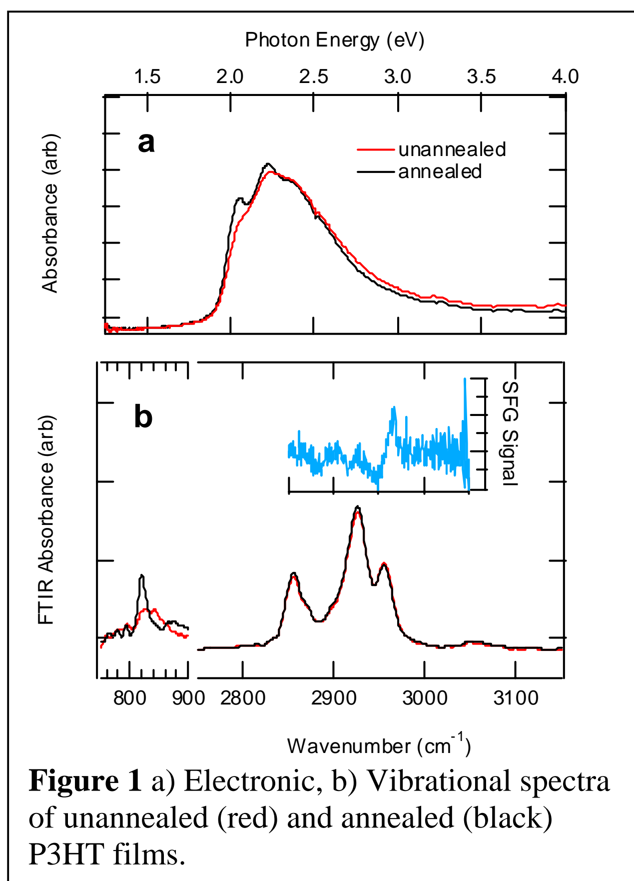


Figure 1 a) Electronic, b) Vibrational spectra of unannealed (red) and annealed (black) P3HT films.

Major Accomplishments: Poly3hexylthiophene (P3HT) has emerged as a prototypical OE material. Transistors made from this material can achieve performance levels close to that of amorphous silicon. Data from traditional structural characterization tools, however, have not shown strong correlations with the electrical performance of P3HT films. Surprisingly, low molecular weight (MW), highly crystalline films have poorer performance than high MW films that appear highly amorphous.

Shown in Figure 1 (a) are transmission absorption spectra for a high MW P3HT film before and after annealing. The fine structure that appears near 2.0 eV after annealing has been attributed to an electronic excitation that spans multiple chains and is indicative of good interchain order. Shown in the main panel of Figure 1 (b) are infrared spectra probing the alkyl side groups (features at 2800-3000 cm^{-1}) and the thiophene ring (823 cm^{-1}). Infrared spectroscopy allows selective study of different parts of the polymer chain, but averages the information over the entire film. The alkyl side chains show little change upon annealing, indicating that, contrary to the behavior in bulk crystals, the alkyl groups do not

drive the ordering of the thin films. Detailed analysis establishes that the alkyl groups are highly disordered. There is significant change in the thiophene ring feature, indicating that the chains adopt a more card-edge stacking structure upon annealing. The inset to Figure 1 (b) shows nonlinear vibrational spectra of the alkyl groups. Unlike infrared spectroscopy, the nonlinear spectroscopy is only sensitive to the surface of the thin film. The presence of the feature near 2960 cm^{-1} indicates that, while the alkyl groups are disordered in the interior of the film, they are highly ordered at the surface. The combination of the three spectroscopies (visible, infrared, and nonlinear) provides a detailed picture of the evolution of the structure that can be related to the electronic properties of the film.

Future Plans: The spectroscopic results will be correlated with direct measurements of the electrical performance of the films to establish the structural characteristics of high performance films. The optical techniques for orientation determination will be validated against direct techniques based on x-ray absorption. Models for the quantitative separation of the buried and free interfaces of ultrathin films via nonlinear optics will be developed and extended to higher order processes such as coherent anti-stokes Raman scattering. All activities will be performed within the context of the FY05 funded NIST Competence Program on *Metrology to Enable the Realization of Organic Electronics Devices.*

Impact: This work demonstrates that vibrational spectroscopies can provide new insight into the structure of OE films and potentially may provide the basis for evaluation and monitoring of OE films by manufacturers.

Title: A new Monte Carlo application for complex sample geometries

Author: Nicholas W. M. Ritchie

Purpose: Performing quantitative microanalysis on micron-sized particles has always been a challenge. The volume of the particle is typically smaller than the electron beam excitation volume and x-ray absorption corrections are complicated by surface topology. Some researchers have approached this problem by approximating the particle as a simple geometric shape such as a cylinder, a rectangular or triangular prism [1]. While this approach is better than applying bulk correction methods, it may be possible to combine topological measurements from multiple imaging detectors to build a more accurate three-dimensional model of the unknown particle. This model could then become the input sample structure for a Monte Carlo simulation. The Monte Carlo simulation could be compared to Monte Carlo simulations of bulk references and the result could be iterated in a manner similar to the iterative correction processed used by the standard ZAF correction scheme. The result is likely to be more accurate quantitative results. However, this scheme relies on the availability of a Monte Carlo model that can handle complex sample geometries.

This work involved developing a library of Monte Carlo simulation routines capable of handling samples of arbitrary geometric complexity.

Major Accomplishments: We have developed and tested a Monte Carlo simulation implemented in platform independent Java code. We have evaluated various different algorithms for electron elastic [2,3] (see figure 1) and inelastic scattering cross section, electron energy loss, fluorescence yield and mass absorption coefficient. For each algorithm class, we have selected the one that we have determined produces the most realistic results. These algorithms have been implemented into a model in which the sample is represented by instances of a generic *Shape* interface[*]. The *Shape* interface represents samples of arbitrary complexity with sufficient detail for the purposes of this model. Implementations of the *Shape* interface have been created for basic shapes such as spheres, blocks and the volume defined by the intersection of an arbitrary number of directed planes. In addition, implementations of the *Shape* interface have been created to represent the union of two or more *Shape*s and the difference of two *Shape*s (the volume of *Shape* A minus the intersection between *Shape* A and *Shape* B). By combining these *Shape*s programmatically, samples of arbitrary complexity can be built from primitive *Shape*s.

Impact: Assigning particles to a descriptive class through quantitative microanalysis is hampered by morphologically induced particle-to-particle variance. It is anticipated that by better modeling the shape of the particle we will be able to reduce particle-to-particle variance and thereby improve our ability to differentiate particles of similar but different materials.

Plans: We plan to use the results from this Monte Carlo simulation to develop and evaluate more computationally efficient analytical expressions for quantifying particulate samples.

References:

1. J. T. Armstrong in *Electron Probe Quantitation,* K. F. J. Heinrich and D. E. Newbury, eds., Plenum Press, New York (1991) pp 261-315
2. Z. Czyzeweski Z, D.O. MacCallum, A. Romig, D. Joy, J Appl. Phys. **68**, 7 (1990) pp 3066-3072
3. A. Jablonksi, F. Salvat, C. J. Powell *NIST Electron Elastic-Scattering Cross-Section Database – Version 3.1.* National Institute of Standards and Technology, Gaithersburg, MD (2003)
4. K. Heinrich in *X-ray Optics and Microanalysis*, R. Castaing, P. Deschamps, J. Philibert, eds. Hermann, Paris (1966) pp 159-167

Result:

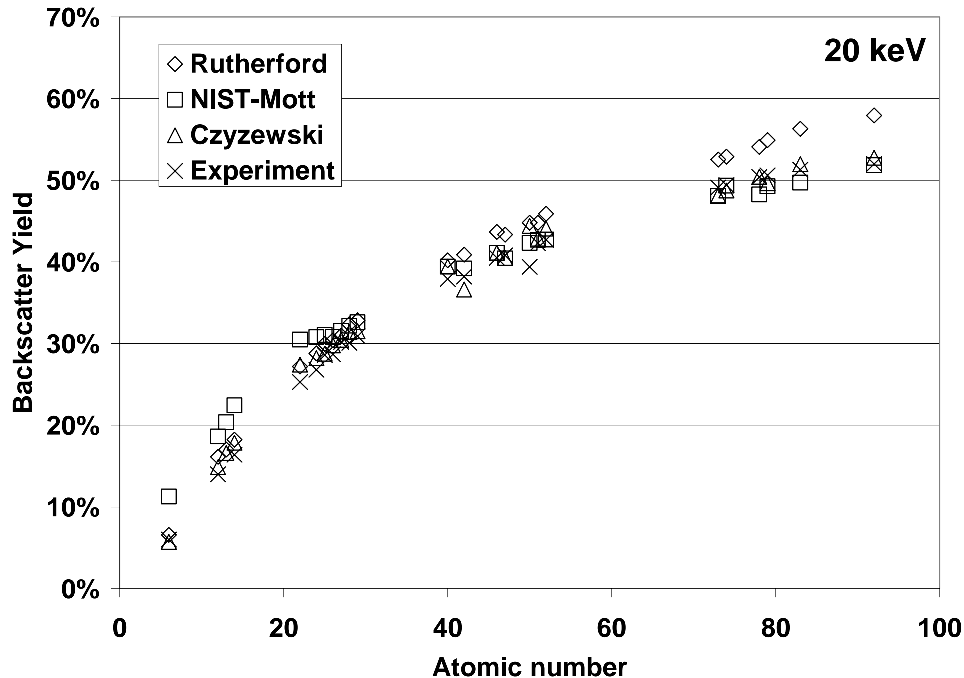


Figure 1: The modeled backscatter yield for various different implementations of the electron elastic scattering cross section compared with measured values from Heinrich [4]. Rutherford corresponds to a simple screened Rutherford cross-section; NIST-Mott [3] and Czyzeweski [3] are different implementations of the Mott cross-section. The Czyzewski cross-section reproduces the experimental results most accurately across the full range of atomic numbers.

* ***Shape* refers to a Java interface (a contract between a classes' user and implementer).**

Title: Controlling "injection barriers" into prototype molecular wires through substrate coupling chemistry

Authors: C.D Zangmeister (836), S. W. Robey (837), R. D. Van Zee (836)

Context: The drive to introduce organic molecular materials into electronic device applications, (organic electronics) is motivated by a number of potentially attractive features, such as ease of fabrication, ability to fabricate on flexible substrates, and the wide extent to which organic materials can be functionalized via organic synthetic methods. A range of applications is foreseen for organic field effect transistors and light emitting diodes including, for instance, flexible displays and other low cost flexible electronics.

In addition to replacing inorganic semiconductors in more or less conventional device architectures, organic systems are also of interest in the more speculative, and potentially more revolutionary, area of "molecular electronics". Here, it is envisioned that the nonlinear characteristics of individual molecules, or small ensembles, will provide the required device functionality, allowing low cost chemical synthetic methods to replace, at least partially, multi-billion dollar semiconductor fabrication lines in the production of nanoscale device structures.

In either application format, charge injection at a molecule-contact interface plays a vital role in controlling transport and, thus, potential device performance. Interfacial charge injection is dictated by chemical bonding and the resulting band line-up between the Fermi level of the contact and transport levels of the molecule. Information relating to band line-up is difficult to obtain using conventional techniques in the case of the single-molecule length-scale systems of interest in molecular electronics. We have employed a combination of one-photon (He I resonance excitation) and two-photon photoelectron spectroscopy, using sub-picosecond Ti:sapphire laser-based excitation, to determine the electronic structure, including injection barriers to both occupied and unoccupied levels, of oligio(p-phenylene-ethynylene)thiol (OPE) self-assembled monolayers, a system that has become a benchmark for theoretical and experimental studies in the area of molecular electronics.

Major Accomplishment: The majority of studies of covalently bound monolayers on metallic surfaces involve thiol-coupling (R-SH) chemistry. Self-assembly of monolayers utilizing thiol chemistry is known to form robust, reproducible monolayers on a variety of metallic surfaces. However, it is important to characterize how the linker group affects the electronic spectra and consequently the band line-up of adsorbed monolayers. Thus, we have undertaken a study of

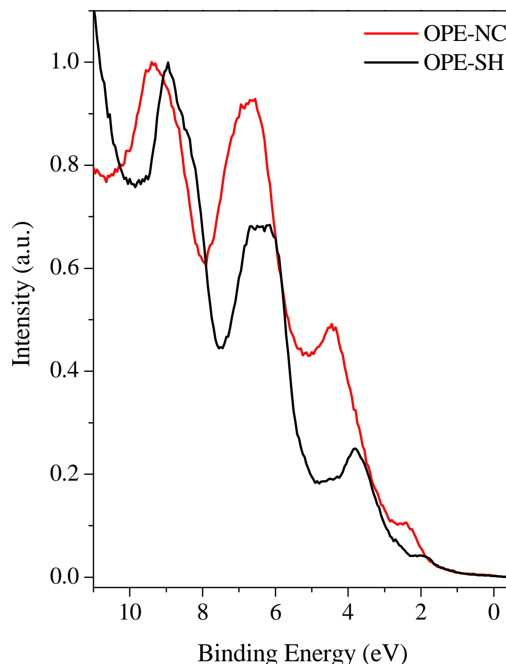


Figure 1: ***One-photon photoelectron***

understanding how the band line-up varies as a function of changing the linking chemistry between the molecule and the surface. One-photon photoelectron spectra given in Figure 1 shows that the substitution of the thiol-linker for isocyanide (R-NC) in OPEs adsorbed on Au shifts the position of the occupied and unoccupied states relative to the Fermi level by ~ 0.5 eV. Such a large variation will have a major impact on charge injection in molecular systems. Models for important aspects of the bonding in these two systems to Au have been developed that help explain the observed behavior.

Future Plans: We aim to build upon our previous studies of understanding the affect molecular structure and linking-group chemistry have on controlling band line-up in covalently bound molecular systems. Our future work will focus on varying the metal onto which the molecule is adsorbed, as well as alkali metal doping of monolayer films.

Impact: These results add important insights to the factors controlling band alignment at metal-organic interfaces, a parameter that plays a critical role in potential applications of organic materials in emerging electronic technologies.

Title: XML for Microanalysis

Author: John Henry J. Scott

Program: Industrial and Analytical Instruments and Services

Vision: The rapid spread of XML technology in many fields of chemical analysis has led to renewed interest in applying XML to the data exchange and data storage problems faced by the microanalysis community. Information about all aspects of a microanalysis experiment (not just spectral results) can be captured by a well-designed Microanalysis Markup Language (MML), which should:

- Enable the free exchange of spectral information among microanalytical instrument users by developing an XML-compliant markup language for spectroscopy data.
- Provide a framework for sharing microanalysis data community-wide to allow more sophisticated theoretical model building and model assessment to take place.
- Create a document format for long-term archiving of microanalysis data that diminishes the effect of "bit-rot" and software decay and helps prevent the loss of data due to lost file formats.

Context: After testing several variation of the markup language and exploring design tradeoffs, multiple working prototypes were implemented to store test data. Independently, the Microanalysis Research Group XML effort began integration into the ASTM E13.15 Animl analytical data markup language project headed by Gary Kramer in the Analytical Chemistry Division. The two projects can interoperate cleanly and a microanalysis component can be added to the Animl project through the development of technique schemas (defined by the Animl framework) based on common microanalysis data acquisition modalities such as scanning transmission electron microscope (STEM), scanning electron microscopy (SEM), and elemental analysis spectroscopies such as electron energy-loss spectroscopy (EELS) and energy-dispersive x-ray spectrometry (XEDS).

Major Accomplishments:

- Implemented multiple working prototypes of Microanalysis Markup Language (MML) based on the original ASCII file format created by the EMSA task force.
- Initiated contact with NIST collaborators Gary Kramer, Dominik Poetz, and Peter Linstrom to integrate concepts from SpectroML and Animl.
- Began contributing to Animl development by attending meetings, studying the schema and framework, and learning the role of ASTM Analytical Data Sub Committee E13.15.

Impact:

- Creation of new microanalysis technique schemas for Animl covering spectroscopies and electron optical scanning techniques (STEM, SEM, Spectrum Imaging) will add significantly to their schema list.

- XML-based metadata already useful for storing information about spectrum imaging experiments to complement LISPIX .rpl files and 3D Chemical Imaging competence.

Future Plans:

- Continue to extend and refine the standard to resolve remaining questions.
- Develop a more detailed model for XML use in spectrum imaging applications.
- Explore the use of XML in building a data pipeline for 3D Chemical Imaging at the Nanoscale.

Title: Quantitative analysis of submicrometer particles in the Scanning Electron Microscope (SEM) utilizing the ζ factor approach

Authors: John A. Small, Nicholas W. M. Ritchie, Jeffery M. Davis

Purpose: The analytical-electron-microscopy (AEM) approach for the quantitative analysis of ultrafine particles, 0.1 nm to 500 nm in size, involves the application of an elemental ratio procedure known as Cliff-Lorimer (CL). This procedure was designed for the AEM analysis of "infinitely" thin samples, for which there is negligible x-ray absorption. [2] The basis for the CL approach is given in equation 1.

$$C_a/C_b = k_{ab} * I_a/I_b \qquad (1)$$

Where k_{ab} is a proportionality constant calculated, using materials of known composition, for a given instrument at a given voltage, C_a and C_b are the concentrations of elements a and b, and I_a and I_b are the measured x-ray intensities.

This investigation was undertaken to determine if the CL approach is applicable to the analysis of ultrafine particles in the SEM at 25 kV-30 kV for which x-ray absorption is not negligible. In this study, a modified CL analysis procedure was employed that includes a correction for x-ray absorption known as the ζ factor. [3]

Major Accomplishments: During the past year we have made a series of measurements on glass shards of known composition that had been ground to produce a large number of ultrafine particles. The particles were analyzed at 25 keV. The results are shown in Figure 1 which plots the Al concentration analyzed by both the CL method and the modified CL which includes the ζ factor. The Al concentration from the CL method at 0.063 wt. fraction has a negative bias compared to the nominal value of 0.074 as a result of not correcting for the absorption of the Al x-rays in the particles. In comparison, after the incorporation of the ζ factor into the CL method the Al wt. percent is 0.075 effectively removing the observed bias and bringing the average concentration more in line with the nominal value.

Impact: The analytical demands associated with technologies for future measurements and standards programs in nanotechnology, the environment, and engineered materials require the analysis of ultrafine particles. Traditionally these small particles have been analyzed in analytical electron microscopes which often require large capital investments in excess of $1,000,000 and have difficult sample preparation procedures. With the increasing need for the analysis of ultrafine particles, the SEM and its counterpart, the electron microprobe, potentially offer a more economical approach.

Future Plans:
This study represents one of two methods we are currently investigating to improving the quantitative analysis of the ultrafine particles. The other approach involves reducing the accelerating voltage of the SEM to 5 kV or less for analysis. The rational for this approach is that the x-ray generation and emission volumes at the low voltage will be contained within the particle volume to a much greater degree than excitation at a higher but more

conventional voltage such as15 kV. Future plans involve the comparison of these the two methods and their effectiveness for the quantitative analysis of ultrafine particles.

References

1. Small, J. A. Journal of Research, 107, #6, 2002, p 555.
2. Cliff, G. and Lorimer, G. W. , J. Microscopy, 103, 1975, p 203.
3. Watanabe, M., Horita, Z. and Nemoto, M. Ultramicroscopy 65, 1996, p. 187.

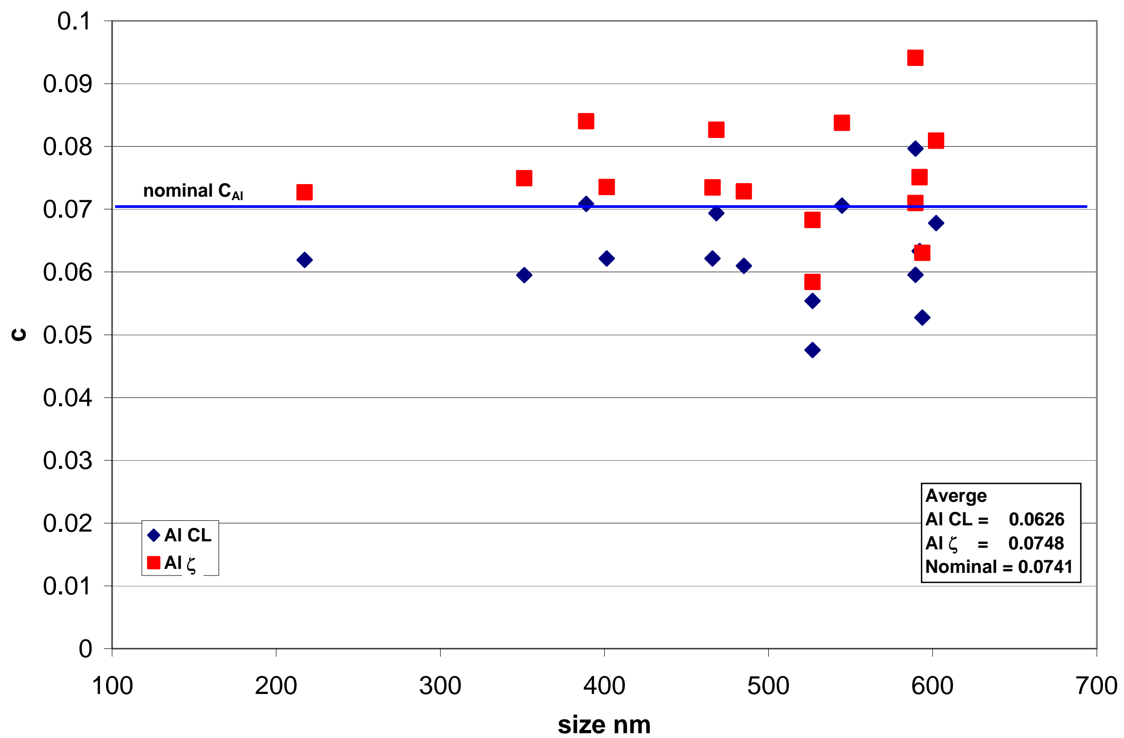


Figure 1. Plot of the Al concentration in ultrafine glass particles analyzed by both the CL method and the modified CL which includes the ζ factor.

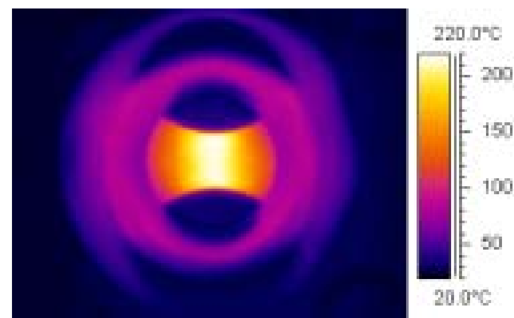
Title: NIST Trace Explosive Vapor Preconcentrator (EVAP) Test Facility

Authors: Mike Verkouteren and Greg Gillen, Div. 837, CSTL

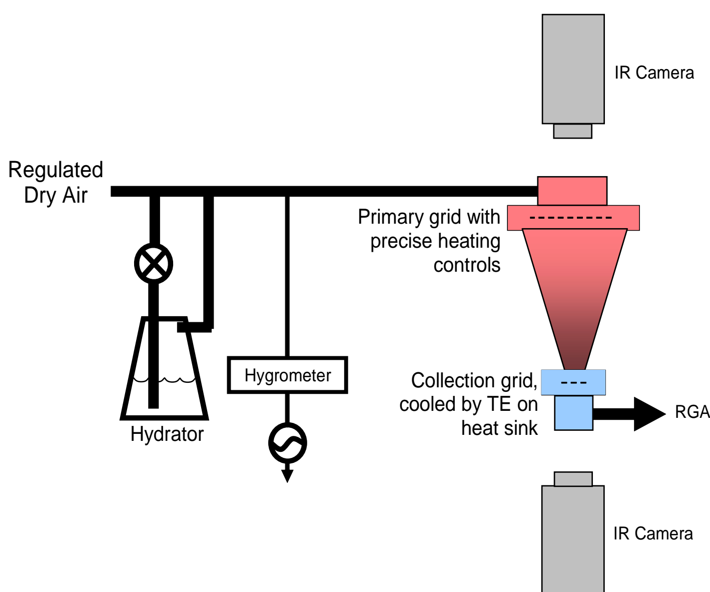
Vision: To improve our Nation's ability to counter terrorism threats by improving the sensitivity of trace explosive detection at airports and other public venues.

Purpose: To establish standards for testing chemical processing technologies that preconcentrate the vapors of RDX, HMX, PETN, TNT, and other explosives.

Context: The standard test system will be used to compare existing methods and materials used in trace explosive chemical preconcentrators, and to provide comprehensive benchmarks for future improvements to preconcentrator technologies. This project is part of a larger effort in the NIST Surface and Microanalysis Science Division focused on strengthening the chemical metrology system that supports the widespread operational deployment of trace explosive detectors needed by first responders and security screeners. This effort is funded by the U.S. Department of Homeland Security (Office of Domestic Preparedness) through the NIST Office of Law Enforcement Standards. Stakeholders include portal/detector manufacturers such as GE Ion Track and Smiths Detection, and the U.S. Transportation Security Agency, which has a broad and immediate mandate to advance and deploy explosive detectors at airports to screen passengers and luggage.



Temporal temperature distribution of a metal substrate, heated resistively to vaporize explosive particles in the EVAP, is revealed by infra-red thermometry. Downstream, explosive vapors are recaptured on a cooled collection grid (not shown).



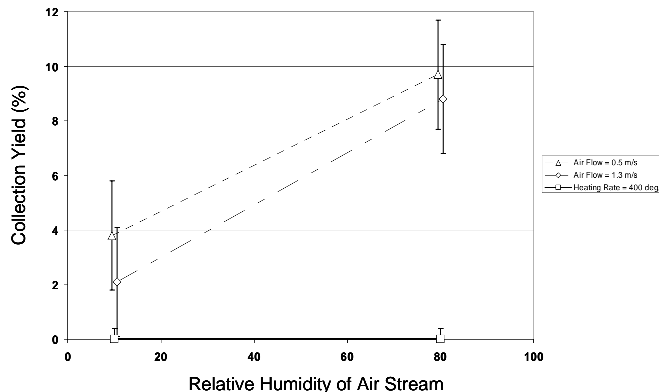
Schematic of EVAP with peripherals that include a regulated air flow controller, hydrator, and hygrometer, through which air of desired humidity (<10% to 90% RH) and flow rate (<1 to 20 LPM) may be supplied. Resistive heating of the primary grid is performed with an operational power supply, where the output voltage and amperage may be adjusted to give the desired heating rate (1 °C/s to 500 °C/s). The EVAP was designed so that the two grids could be monitored by infra-red (IR) thermometry through BaF_2 (IR-transparent) windows. Other components include a thermoelectric (TE) Peltier cooling module and an interface for future residual gas analysis – i.e., measurements of explosive vapors in the air stream that were not condensed on the collection grid.

Major Accomplishments: The major technical challenge involved the design and fabrication of a robust system that integrated the ability to monitor multiple aspects of performance, allowed flexibility of configuration, and was fairly easy to operate. Demonstration of capabilities involved determining the collection efficiency of the EVAP with respect to explosive type, heating rate, and airstream velocity and humidity. These four variables all proved to be

significant. Under the operational ranges tested, RDX – but not PETN or TNT – was collected. Collection was enhanced at low heating rates, low air flow rates, and high airstream humidity levels.

Future Plans: Morphology and chemical derivation of collector surfaces will be explored, as well as over 25 operational variables that may govern the explosive collection efficiency of vapor preconcentrators. We have designed fractional factorial experiments to explore the significance and interrelationships among these variables. In FY05, measurements and multivariate analysis will be performed to characterize comprehensively the EVAP performance.

Program: Forensics and Homeland Security



Results for vapor collection of RDX on 316L stainless steel mesh at 70 ºC. Collection was enhanced by slow heating rate (20 deg/s), low air flow (0.5 m/s face velocity on collector), and high water vapor content of air stream (relative humidity = 80 % at 20 ºC). Error bars are standard uncertainties based on reproducibility of replicated ion mobility spectrometry measurements.

Title: In-Situ Characterization of Additives Governing Copper Electrodeposition

Authors: M. L. Walker (837), L. J. Richter (837) and T. P. Moffat (MSEL)

Context: One of the critical issues facing the microelectronic/semiconductor industry is the robust fabrication of "on-chip" interconnections (wiring) between transistors and related devices. Copper has replaced aluminum as the metal of choice for such interconnects, due to its lower resistivity and superior electromigration characteristics. Interconnections are formed by electrodepositing copper into lithographically-defined sub-micrometer wide features (trenches and vias). The feature filling process occurs by superconformal or "bottom-up" growth that derives from a competition between electrolyte additives, i.e. inhibitors and catalysts, for available surface sites. A representative additive package to plating baths contains polyethylene glycol (PEG), chloride(Cl^-) and sulfonate-terminated disulfides such as $Na_2[SO_3(CH_2)_3S]_2$ (SPS). Inhibition is provided by PEG/Cl^- while disruption of the PEG species by SPS/Cl^- leads to acceleration of the metal deposition. Incorrectly formulated baths can lead to uncontrolled electrodeposition, resulting in faulty interconnect creation and poor device performance. The PEG/Cl^- system was studies to more fully characterize synergies between bath components and probe the utility of spectroscopic ellipsometry (SE) for the *in situ* evaluation of electrodeposition. SE, a non-destructive optical technique capable of measuring optical characteristics of a surface, is routinely used in the semiconductor industry to evaluate wafer quality.

Major Accomplishments: Commercially available SE instrumentation was modified to probe the effect of additives on metal substrates in liquid-based environments similar to the electrolytic plating baths used in the industry. The result, *in-situ* dynamic SE, can accurately measure film thickness with better than 0.1 nm accuracy under certain conditions. The formation of a film upon the addition of PEG and Cl^- was observed as shown in Figure 1.

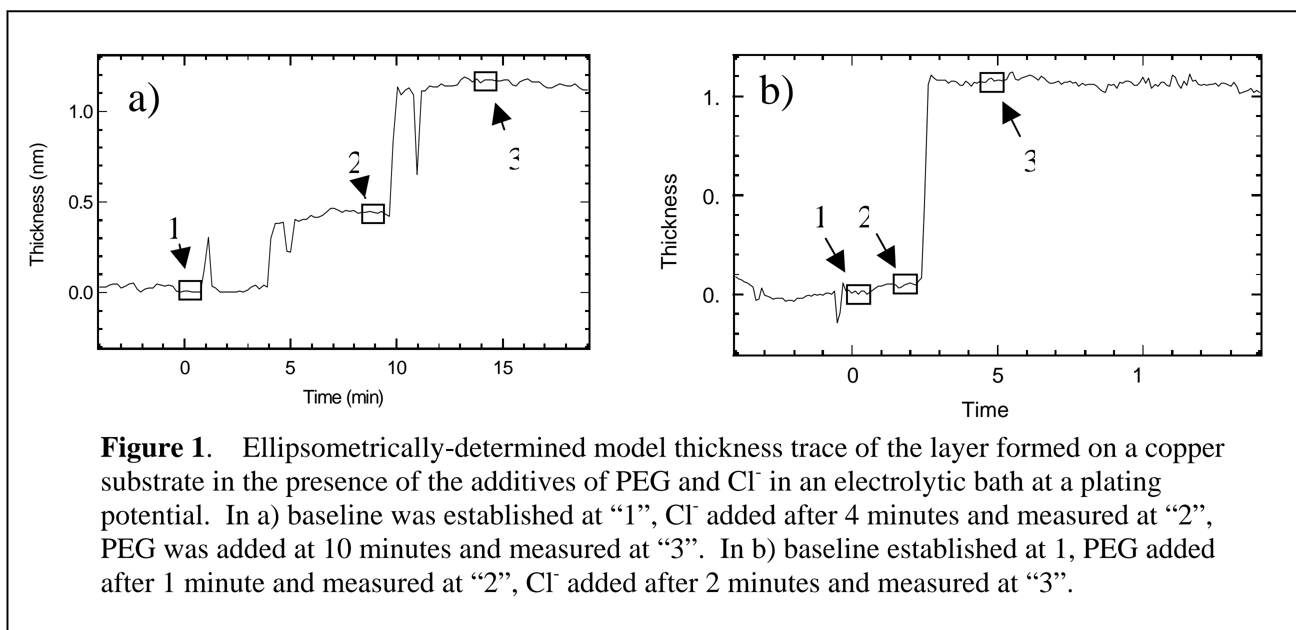


Figure 1. Ellipsometrically-determined model thickness trace of the layer formed on a copper substrate in the presence of the additives of PEG and Cl^- in an electrolytic bath at a plating potential. In a) baseline was established at "1", Cl^- added after 4 minutes and measured at "2", PEG was added at 10 minutes and measured at "3". In b) baseline established at 1, PEG added after 1 minute and measured at "2", Cl^- added after 2 minutes and measured at "3".

The results show the presence of Cl^- is necessary for the formation of a film, but a film eventually forms regardless of additive order. The adsorbed PEG film thickness is approximately 0.5 nm, consistent with a single layer of helically-wound PEG. Additional studies on gold and silver substrates established that chelation of copper ions is not necessary for film formation.

Future Plans: Studies on the three component PEG/Cl^-/SPS system are planned to build on the insights gained from the PEG/Cl^- system. Additionally, the use of other materials such as ruthenium as substrates for copper electrodeposition applications will be examined

Impact: These results have relevance to the industrial practice of electrodepositing metals for on-chip metallization as well as printed circuit board applications, and the study is part of efforts at NIST designed to support the microelectronics/semiconductor industry. The method and measurement have been submitted for publication.

Publications: M. L. Walker, L. J. Richter and T. P. Moffat, "*In-Situ* Ellipsometric Study of PEG/Cl^- Co-adsorption on Cu, Ag and Au", submitted to *J. Electrochemical Soc.*

Title: Characterization of Silicon Semiconductor Electronics Using SIMS Backside Depth Profile Analysis

Authors: E. Windsor (837), G. Gillen (837), P. Chi (837), D. Bright (837), and J. Bennett (International SEMATECH)

Vision: As silicon semiconductors continues to shrink, greater demands are placed upon the metrology techniques used to characterize these materials. If downscaling proceeds according to the schedule outlined by the International Technology Roadmap for Semiconductors, many metrology methods in current use will not have sufficient resolution to characterize future generation semiconductors. We envision that backside sample preparation combined with novel instrumental techniques such as C_{60}^{+} cluster ion bombardment will extend the utility of SIMS measurements to the characterization of future generation silicon semiconductors.

Purpose: The purpose of this work is to improve SIMS depth resolution of semiconductors. We accomplish this through the combined use of backside sample preparation, secondary ion image depth profiling and image analysis techniques.

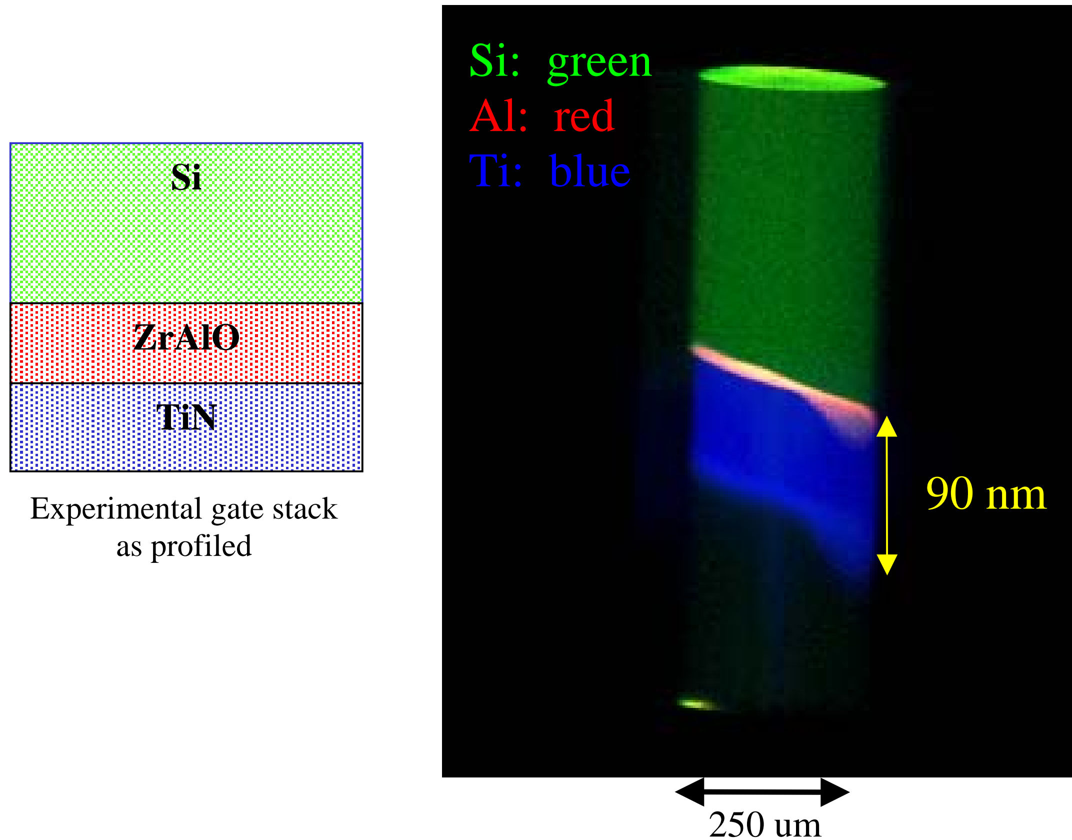
Context: The analytical microscopy group is working together with the Office of Microelectronic Programs at NIST to develop metrology techniques for the characterization of future generation semiconductors. SIMS is a useful characterization tool because the technique has high analytical sensitivity and good depth resolution. State of the art SIMS instruments are capable of reaching sub-micron depth resolution. Such resolution however, is often not achieved when analyzing semiconductors due to limitations imposed by the samples themselves. This is particularly evident in the characterization of shallow dopant profiles and the investigation of diffusion of material through thin gate dielectric films. For both these examples, the analysis area is the ultra-shallow region of the silicon substrate. This region is buried below numerous layers of different materials that were deposited during the manufacturing process. Using SIMS to analyze the area of interest, one must first sputter through these different processing layers. Depth resolution is degraded while sputtering through these layers because of the development of surface topography (especially when sputtering through polycrystalline materials) and the occurrence of knock-on ion beam mixing.

With backside depth profile analysis, high depth resolution is maintained by analyzing the sample from the back (substrate) side rather than the front side. This eliminates the need to sputter through the multiple processing layers on the front side of the wafer.

Major Accomplishments: We have developed a backside sample preparation method that uses mechanical grinding and polishing to remove the silicon substrate prior to SIMS analysis. The method can be applied to a variety of different samples including fully processed, patterned wafers.
We have prepared three-dimensional chemical images that illustrate artifacts produced during the grinding and polishing procedure. This was accomplished using secondary ion image depth profiling techniques to sequentially collect a stack of images during ion

sputtering. These images were then combined to produce three-dimensional chemical images. The image below clearly shows the artifact of inclined polishing; the plane of polish is inclined relative to the surface of the sample. If not corrected, this artifact will degrade the resolution of our SIMS analysis.

By applying advanced image analysis techniques to the image stack, we minimized the effect of inclined polishing and improved the depth resolution of our SIMS analysis.



Experimental gate stack as profiled

Impact: By improving depth resolution, backside SIMS depth profile analysis should extend the utility of SIMS measurements to the characterization of future generation semiconductor electronic devices.

Future Plans: Future plans include combining backside sample preparation with C_{60}^{+}cluster ion SIMS depth profiling to further improve the depth resolution of SIMS measurements.