

Surface and Microanalysis Science - Table of Contents

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SURFACE AND MICROANALYSIS SCIENCE DIVISION OVERVIEW

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 several 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

- Conducts theoretical and experimental research concerning chemical processes at surfaces and interfaces with emphasis on systems relevant to electronic, polymer and photonic applications.
- Develops and applies surface sensitive diagnostics involving laser-based sources, and proximal probes with fine 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
- Performs calculations to investigate the interactions of atoms, molecules, electrons, and radiation with surfaces and interfaces.
- Applies advanced measurement methods to critical problems in semiconductor, polymer, electronic, and nanoscale science.

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, such as 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 procedures for layered specimens and thin films:

- **R.B. Marinenko** with Z. Samardžija, S. Bernik, B. Malič and M. Čeh: *Electron Probe Characterization of KNbO₃ and NaNbO₃ Single Crystals for use as Quantitative Microanalysis Reference Materials (see also - IAIS).*
- **T. Jach:** *Comparison of Gate Oxide Thicknesses using Spectroscopic Ellipsometry, Grazing Incidence X-Ray Photoelectron Spectroscopy, and Neutron Reflectometry.*
- **D. Simons** with R. Paul (839) W. Guthrie (898) and J. Lu (898): *Development of Phosphorous Ion Implant in Silicon Depth Profile Standard (see also - IMS).*

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.

The need to assess chemical information beyond that of composition and phase is possibly most evident for emerging applications in areas including polymer nanocomposites, and nanoscale device optimization. Improvements in sensitivity coupled with reduction in sample degradation are being pursued in Secondary Ion Mass Spectrometry to broaden the impact of this technique to include polymer and other "soft" surfaces. Innovative scanned probe methods are being developed in our Combinatorial Methods Competence Project to combine optical contrast mechanisms with near-field measurements. The Division has developed capabilities in visible, Raman, and infrared near-field methodologies, and has developed collaborative efforts with MSEL, BRFL, 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:** *Growth of Oriented ZnO Nanowires on Sapphire and Gallium Nitride.*
- **J.H.J. Scott and J. Conny:** *Trace Nanoanalysis Using Hyperspectral Imaging (see also – MicroE).*
- **S. Turner, D. Bright and V.L. Karen (852):** *Progress Towards Development of an Improved Method of Phase Identification by Selected Area Electron Diffraction (see also – IAIS).*
- **C. Mahoney, S. Roberson and G. Gillen:** *Cluster SIMS Depth Profiling of a Polymer Drug Delivery System (see also – P&B).*
- **J.W. Gadzuk:** *Hot Electron Chemicurrents Produced in Chemical Processes at Surfaces: A Theoretical Model.*
- **J.D. Batteas, J.C. Garno, C.A. Gonzalez (838), C.A. Hacker (812), L.J. Richter, S.W. Robey, C.D. Zangmeister (836), and R.D. van Zee (836):** *Molecular Electronics Metrology (see also – 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

- **J.R. Verkouteren:** *Particle Size Characteristics of Trace High Explosives: PETN and RDX (see also - FHLS).*
- **R.A. Fletcher, G. Gillen and E. Ferguson:** *Particle Removal Rates from Planar and Cloth Surfaces; A Critical Step in Airport Security (see also - FHLS).*
- **J.T. Armstrong and J.A. Small:** *Development of SEM-EDS Analysis Procedures for C, N and O to Enable Characterization of Explosives Particles, Polymeric and Organic Materials (see also - FHLS).*
- **G. Gillen:** *Automated Analysis of Organic Particles using Cluster SIMS (see also - FHLS and ETS).*
- **S. Turner, J.R. Sieber (839), T. Vetter (839), R.L. Zeisler (839), D.A. Becker (839), B.H. Toby (856), J. Kelly (852), R.A. Fletcher, E.S. Windsor, M. Davis (Cal Tech), S. Yang (U.C. Davis), A. Navrotsky (U.C. Davis), S.D. Leigh (898), and R.R. Cavanagh:** *Characterization of Chemical Properties, Structural Parameters and Particle Size Distribution of Three Zeolite Reference Materials.*

4. Chemical Characterization of Materials: Surfaces and Interfaces

- **J.R. Verkouteren:** *Refractive Index Measurements of FBI Liquid for Forensic Glass Particles (see also – FHLS).*
- **L.J. Richter, C.S.-C Yang (844), J.C. Stephenson (844), and K.A. Briggmann (844):** *Characterization and Control of Gel-Fluid Phase Transitions in Supported Phospholipid Monolayer Films (see also – BMTLS).*
- **M.S. Wagner:** *Energy Dependence of SF₅⁺ Bombardment of PMMA Films Studied using ToF-SIMS (see also – P&B).*
- **S. Wight:** *Identification of Contaminants in Surface Films by Scanning Auger Microscopy.*
- **J.T. Armstrong:** *Materials Evaluation and Database Tabulation for Fundamental Parameters and Algorithms used for Quantitative Electron Probe Microanalysis.*
- **C. J. Powell, A. Jablonski (Poland), and F. Salvat (Spain):** *Evaluation of Electron Elastic-Scattering Cross Sections (see also - IMS).*
- **C. J. Powell, W. S. M. Werner (contractor), and W. Smekal (contractor):** *Development of New Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) (see also – IMS).*

5. Analytical Tools for High-Throughput Experimentation in Materials and Chemical Manufacturing

- **D.E. Newbury:** *Improving Limits of Detection in Microanalysis with High Speed X-Ray Spectrometry (SDD-EDS).*
- **C.A. Michaels, D.B. Klinedinst, E.S. Windsor,** and D. Bruce Chase (DuPont): *Characterization of Spatial Variations in Nomex® Fiber Crystallinity with Confocal Raman Microscopy.*
- **D.S. Bright:** *Descriptive Terms of Particle Appearance for Search and Classification (see also - FHLS and ETS).*

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:

- **J.M. Conny:** A Question of Accuracy: How Does Thermal-Optical Analysis for Climatically Important Black Carbon in Atmospheric Soot Behave Optically?

ANNUAL HIGHLIGHTS

Significant efforts during FY03 were focused on preparation for the relocation of all Division activities to the new laboratory building that is scheduled to occur early in calendar year 2004. Working closely with CSTL management and with other NIST laboratories, we have been able to identify resources to allow the purchase of a focused ion beam facility and an advanced Analytical Electron Microscope. Both of these new equipment items will be integrated with existing Division facilities as we occupy our new home the **Advanced Measurement Laboratory**. These pieces of new instrumentation will be critical for keeping NIST at the forefront of nanocharacterization expertise.

Division staff members have been involved with the development of shared appreciation for the measurement needs that will accompany applications that incorporate **nanoscale science and engineering**. Appropriate nanoscale characterization tools will be required to meet the needs of industry, and the Division strives to stay abreast of those emerging needs. To this end, Division staff members have participated in the *Technology Vision 2020* effort under the Council for Chemical Research entitled "Nanotechnology Road Map". The Division also co-sponsored a *Nano-analysis* Session at the American Chemical Society 226th National Meeting in September 2003. Furthermore, the Division helped organize industry-focused meetings in this area including the *Nanotechnology Business Roadmap for Industry* in October 2002 and is helping to plan for *Nanocommerce 2003* that will be held in FY 04. These and similar efforts assist in keeping Division efforts in nanoscale characterization in tune with national needs assessments.

The Division has also been active in drawing attention to the impact of nanoscale chemical characterization in areas of environmental concern (nano particles), in electronic device characterization (sub 130 nm technology and molecular electronics) and in nanomaterials characterization. One example of these interactions was the co-organization (with MSEL and EEEL) of the NIST-NASA Workshop on Purity and Dispersion Measurement Issues in Single Wall Carbon Nanotube Materials that was held at NIST's Gaithersburg site in the Spring of 2003.

Events over the past two years have led the Division to embark on a major effort in support of **Homeland Security**. FY 2003 witnessed a significant 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. This effort benefits significantly from strong interactions with the Transportation Security Administration.

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 Bruyeres 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.

An additional aspect of the Division's efforts in homeland security is exemplified by our efforts in *Gas Mask Verification* for the Chemical Biological Defense Committee of the Joint Services Calibration Coordination Group. The measurement expertise that has supported military gas masks has been directed at first responder needs this year.

Two **Competence Projects** that were funded by the NIST Director have just completed their third year of funding. The *Molecular Electronics* project is a joint effort with the Process Measurements and the Physical and Chemical Properties Divisions of CSTL and the Semiconductor Electronics Division of EEEL. This effort 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. Also in its third year, the Competence Project - *Polymer Thin Films: A Testbed for Combinatorial Methods*- is a joint effort with the Polymers Division of MSEL. This 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. At the end of FY03, the Division learned that its competence proposal for *3D Chemical Imaging at the Nanoscale* had been funded. This effort will bring together existing expertise from the Electron and Optical Physics Division in PL, the Metallurgy Division in MSEL, 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.

Fiscal year 2003 saw the release of four updates to **databases** in the Surface Analysis Data Center. Release of Versions 3.3 and 3.4 of SRD 20 X-ray Photoelectron Spectroscopy Database marked the ongoing effort to incorporate new data as it appears in the literature. Version 3.3 contains approximately 3,000 additional data records and Version 3.4 contains a new method for retrieving and displaying data. Release of Version 3.0 of SRD 64 - NIST Elastic-Electron Scattering Cross-Section - brought two major improvements: (1) cross sections and related data were computed from a more reliable atomic potential, and (2) the upper energy limit was increased from 20 keV to 300 keV. Version 3.1 contains two minor corrections.

STAFF RECOGNITION:

Stephan Stranick – won the American Chemical Society's Division of Analytical Chemistry's *Arthur F. Findeis Awards for Achievement by a Young Analytical Scientist*. He received the award in September in recognition of his extraordinary contributions in the area of near-field chemical-imaging microscopy.

Richard Cavanagh – was elected a Fellow of the American Vacuum Society (AVS) in recognition of his contributions to the understanding of energy –transfer rates and pathways for molecular processes at surfaces.

Dale Newbury and Ryna Marinenko - were nominated for the CSTL Technical Achievement Award in FY 2003. Dale and Ryna edited and contributed to the Special Issue of the NIST Journal of Research entitled "*Accuracy Barriers of Quantitative Electron Beam X-ray Microanalysis.*" This issue captured the proceeding of NIST-MAS Workshop, *The Accuracy Barrier in Quantitative EPMA and the role of Standards* that was held in 2002 on the NIST Gaithersburg campus. The Nov/ Dec 2002 issue dedicated 244 pages to the quantitative measurement issues associated with electron beam microanalysis, and will allow the insights gained from this meeting to reach beyond the original 125 participants who attend the workshop either in person or through the link that was established to Webcast the meeting. Their innovative approach to dissemination of the content of this workshop marked a significant incorporation of modern technologies in conveying Division activities to a broader user base.

Newbury, D.E., "*Barriers to Quantitative Electron Probe X-ray Microanalysis for Low Voltage Scanning Electron Microscopy,*" J. Res. NIST, **107** (2002) 605-619.

Marinenko, R.B., "*NIST Standards for Microanalysis and the Certification Process,*" J. Res. NIST **107** (2002) 687-91.

INTERACTIONS:

The Division is involved in advisory and technical efforts with other government organizations including EPA, IAEA, NSF, TSA, 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: Charles Evans & Assoc., Dow Chemical, Dow Corning, DRI, DuPont, ExxonMobil Chemical, Honeywell, McCrone Assoc., MTS Systems Corporation, Noran, Peabody Scientific, Pfizer, Photon Imaging, Schafer Vallecitos Laboratories, SRI, 3M, Visteon, and XOS, Inc.

Identification of Contaminants in Surface Films by Scanning Auger Microscopy

Authors: Scott Wight

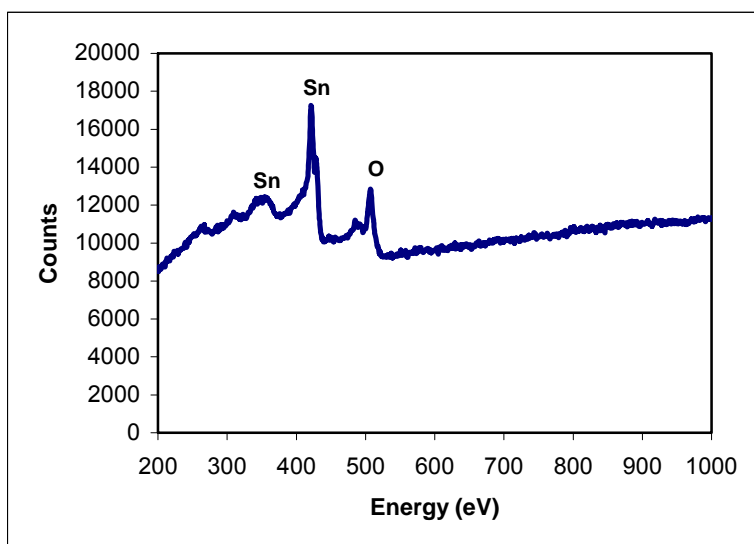
Program: Chemical Instruments-HTS

Abstract: The surface specificity of Auger microscopy is ideally suited to identify contaminant films and particles on surfaces. In the electronics industry, as devices continue to shrink, scanning Auger microscopy is being more widely utilized to identify contaminants. In this study, scanning Auger microscopy has been applied to the identification of contaminants on the surfaces of two technologically important materials. In these studies, rapid identification of contaminants has been demonstrated with a long-term goal of rapid quantitative analysis of contaminant films and particles.

Purpose: NIST's analytical scanning Auger microscope (ASAM) has been applied to two specific measurement challenges. 1) It was used to identify the contaminant precipitates in tin-copper electrodeposited films on copper substrates. These films are an important step towards lead-free solders for the microelectronics industry. 2) The ASAM was used to identify and provide a maximum thickness for the contamination areas on a copper plate used for the proposed new NIST capacitance standard based on the charge of the electron.

Major Accomplishments: The contaminate particles in the tin-copper electrodeposited films were identified as tin oxide precipitates by scanning Auger microscopy (see Fig 1). Prior to analysis, the area of interest was carefully cleaned, by low energy ion etching, to remove the ubiquitous organic contamination that otherwise masks the composition of the particles. In the cleaning process it was necessary to strike a critical balance between removing the oxygen and organic contaminants that had adsorbed onto the surface during transport in air and not removing the particles before they are analyzed. Figure 1: Auger spectrum of contaminant particle on Sn-Cu film.

The contamination films on the copper plate were identified as mixed hydrocarbon and



oxide with a thickness of ≤ 3 nanometers. The thickness was determined by argon ion sputtering with a calibrated etch rate for different lengths of time until the carbon and

oxygen peaks were completely removed from the Auger spectrum. This was repeated at multiple locations on the surface of the copper plate to assess the variability and determine the maximum contamination film thickness.

Impact: In both examples discussed above, the Auger results have provided the NIST researchers with the feedback they needed to continue development of important new technologies in the field of microelectronics.

Future Plans: Scanning Auger microscopy will continue to be applied to applications that require surface selective compositional information. The goal is to provide quantitative chemical composition information for particle and thin film characterization problems by scanning auger microscopy.

Cluster SIMS Depth Profiling of a Polymer Drug Delivery System

Authors: Christine Mahoney, Sonya Roberson and Greg Gillen

Program: Pharmaceuticals and Biomanufacturing

Abstract: Secondary Ion Mass Spectrometry (SIMS) has proven to be a useful tool in the analysis of drug delivery systems. With SIMS, the distribution of both drugs and excipients within a drug delivery system can be determined with a high degree of spatial resolution (<1 μ m) and sensitivity (as low as ppm) when compared to other analytical methods (such as Raman or IR). SIMS analysis of drug delivery systems using polyatomic or cluster primary ion beam is of considerable interest. Cluster primary ion bombardment of certain organic materials results in significant improvements (up to 100 fold) in characteristic molecular secondary ion yields and a reduction primary beam-induced damage. The decrease in beam-induced damage coupled with an increased sputter rate has led to the ability to depth profile through some organic materials without the characteristic rapid signal decay observed with monoatomic primary ion sources. More importantly, depth profiling through polymer samples has been achieved for the first time, though with limited success. This project was designed to explore the feasibility of cluster SIMS for depth profile analysis of model drug delivery systems with an emphasis on polylactic acid based systems. Molecular depth profiles obtained from polylactic acid films doped with a model drug show very little degradation in molecular signal as a function of increasing SF₅⁺ primary ion dose. These results indicate that in these model systems, the distribution of a drug as a function of depth can be monitored.

Purpose: The purpose of this work was to determine the feasibility of utilizing cluster primary ion SIMS to monitor the distribution of a drug as a function of depth in a model drug delivery system. SIMS has already proven to be a powerful tool in the spatial analysis of drug delivery materials. However, with the advent of cluster primary ion beams, such as SF₅⁺, the ability to determine the distribution of a drug as a function of depth becomes feasible for the first time. This new capability will aid pharmaceutical companies in the development of new drug delivery systems, including complex controlled release formulations, which are highly dependent upon the homogeneity and diffusivity of the materials involved.

Major Accomplishments: The behavior of a series of poly(lactic acid) (PLA) films doped with varying concentrations of the model drug 4-acetamidophenol, under SF₅⁺ primary ion bombardment, was investigated in order to determine whether the distribution of the drug could be measured as a function of depth. Figure 1 shows a typical depth profile of a PLA film containing 20% by weight 4-acetamidophenol (~200 nm) spun cast onto a Si wafer. The figure shows that the secondary ion intensities associated with both polymer and drug moieties remain stable with increasing SF₅⁺ primary ion dose. These secondary ion intensities remain constant until reaching the PLA / Si interface, at which point both PLA and 4-acetamidophenol intensities drop, corresponding to an increase in Si secondary ion intensity. The polymer film / Si interface was surprisingly well defined (~10-15 nm depth resolution) which may imply that sputter-induced topography formation was not a significant limitation. Several other biodegradable materials including polyglycolic acid, poly(lactic glycolic) acid, polycaprolactone and polyethylene glycol were also depth profiled, with similar results to PLA. These results suggest that the common main chain structural unit of these polymers, R-CO-O-R, facilitates beam-induced bond cleavage and damage removal. More importantly, these results indicate that in these particular model systems, the

distribution of the drug as a function of depth can be monitored when applying cluster SIMS.

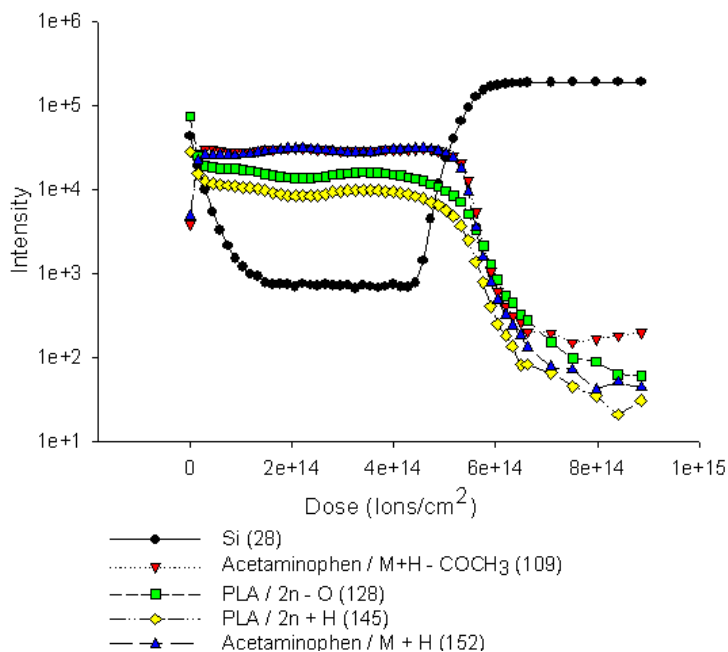


Figure 1. SIMS depth profile of a PLA film containing 20% by weight 4-acetamidophenol (~200 nm) spun cast onto a Si wafer. The film was analyzed using SF₅⁺ primary ion bombardment.

Impact: SIMS has already been shown to have great potential in the field of drug delivery as a means to determine the spatial distribution of a drug in a drug delivery system. With the application of cluster SIMS it is possible to determine the distribution of a drug as a function of depth. The application of cluster SIMS for characterization of drug delivery systems may help pharmaceutical companies with detection of drug migration and diffusion and may be useful as a means of quality control.

Future Plans: Future plans involve utilizing the signal enhancement obtained with cluster primary ion beams for improvements in secondary ion imaging of drug delivery systems. Once this is achieved, we will explore the possibility for 3D molecular characterization of these systems. The utilization of SIMS for quantification of drugs in complex drug delivery matrices is also an important part of our future research plans. Collaborations with key pharmaceutical manufacturers will be initiated so that we can utilize the cluster SIMS capability for applied problem solving and to help with the characterization and development of new drug delivery materials.

Evaluation of Electron Elastic-Scattering Cross Sections

Authors: C. J. Powell; A. Jablonski (Poland); F. Salvat (Spain)

CSTL Programs: Industrial and Analytical Instruments and Services Program

Abstract: Differential cross sections for the elastic scattering of electrons by atoms are needed for modeling the transport of electrons in materials by Monte Carlo simulations and other means. Such transport calculations are needed to improve the accuracy of surface analyses, bulk analyses, and thin-film analyses of inhomogeneous samples by the techniques of Auger-electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), electron-probe microanalysis (EPMA), and analytical electron microscopy (AEM). The cross sections are also needed for similar transport calculations in other applications including radiation dosimetry, radiation therapy, radiation processing, radiation protection, and electron-beam lithography. Since cross sections have been measured only for a limited number of atoms and electron energies, it is necessary to make use of calculated cross sections in the transport calculations.

We made a comprehensive evaluation of differential cross sections for elastic scattering of electrons by neutral atoms that were calculated from two commonly used atomic potentials. Comparisons were also made of the calculated cross sections with measured cross sections. From an analysis of certain quantities derived from the calculated cross sections and those obtained by other means, we concluded that atomic differential cross sections were empirically useful for simulations of electron transport in solids for electron energies above about 300 eV.

Purpose: To provide needed data and reliable models for more accurate surface, interface, bulk, thin-film and particulate analyses by AES, XPS, EPMA, and AEM.

Major Accomplishments in FY2003: An extensive analysis was made of differential cross sections (DCSs) for the elastic scattering of electrons by neutral atoms that were derived from two commonly used atomic potentials: the Thomas-Fermi-Dirac (TFD) potential and the Dirac-Hartree-Fock (DHF) potential. DCSs from the latter potential are believed to be more accurate. This analysis is to be published in a forthcoming issue of the *Journal of Physical and Chemical Reference Data*.

We compared DCSs for six atoms (H, Al, Ni, Ag, Au, and Cm) at four energies (100 eV, 500 eV, 1000 eV, and 10 000 eV) from two NIST databases in which DCSs had been obtained from the TFD and DHF potentials. While the DCSs from the two potentials had similar shapes and magnitudes, there could be pronounced deviations (up to 70%) for small scattering angles for Al, Ag, Au, and Cm. In addition, there were differences of up to 400% at scattering angles for which there were deep minima in the DCSs; at other angles, the differences were typically less than 20%. The DCS differences decreased with increasing electron energy.

DCSs calculated from the two potentials were compared with measured DCSs for six atoms (He, Ne, Ar, Kr, Xe, and Hg) at energies between 50 eV and 3 keV. For Ar, the atom for which measured DCSs are available over the largest energy range, there was good agreement between the measured DCSs and those calculated from the TFD and DHF potentials at 2 keV and 3 keV, but the experimental DCSs agreed better with the DCSs from the DHF potential at lower energies. A similar trend was found for the other atoms. At energies less than about 1 keV, there were increasing differences between the

measured DCSs and the DCSs from the DHF potential. These differences were attributed to the neglect of absorption and polarizability effects in the calculations.

We also examined the extent to which three quantities derived from DCSs varied depending on whether the DCSs were obtained from the TFD or DHF potential. First, we compared calculated and measured elastic-backscattered intensities for thin films of Au on a Ni substrate with different measurement conditions, but it was not clear whether DCSs from the TFD or DHF potential should be preferred. Second, we compared electron inelastic mean free paths (IMFPs) derived from relative and absolute measurements by elastic-peak electron spectroscopy and from analyses with DCSs obtained from the TFD and DHF potentials. In four examples, for a variety of materials and measurement conditions, we found differences between the IMFPs from the TFD and DHF potentials ranging from 1.3% to 17.1%. Third, we compared mean escape depths for two photoelectron lines and two Auger-electron lines in solid Au obtained using DCSs from the TFD and DHF potentials. These mean escape depths varied from 4.3% at 70 eV to 0.5% at 2016 eV at normal electron emission, and became smaller with increasing emission angle.

Although measured DCSs for atoms could differ from DCSs calculated from the DHF potential by up to a factor of two for electron energies less than 1 keV, we found that the atomic DCSs were empirically useful for simulations of electron transport in solids for electron energies above about 300 eV. This unexpected result appears to be due to the smaller absorption correction (i.e., smaller total inelastic scattering cross sections) in the calculated DCSs for solids than for the corresponding atoms. The atomic DCSs could also be useful for energies down to at least 200 eV if relative measurements were made.

Impact: This analysis has provided quantitative information on the extent of differences between DCSs calculated from the TFD and DHF potentials, the extent of differences between calculated and measured DCSs, and the extent of differences between three quantities derived from DCSs and the corresponding values obtained by other means. This information can be used to estimate uncertainties of DCSs derived from the DHF potential (these DCSs are included in Version 3.0 of the NIST Electron Elastic-Scattering Cross-Section Database - SRD 64 - that was released in FY2003) and of quantities derived from the DCSs.

Future Plans: We plan to investigate the magnitude of the absorption correction in DCSs for elastic scattering of electrons in amorphous or polycrystalline solids. We expect that it will then be possible to calculate DCSs for solids in the same way as now done for atoms. If successful, this development will allow Monte Carlo and other simulations of electron transport in solids to be made with DCSs that will be more reliable than those for the corresponding atoms.

Particle Removal Rates from Planar and Cloth Surfaces; a Critical Step for Providing Airport Security

Authors: Robert Fletcher, Greg Gillen and Erin Ferguson (Div. 837)

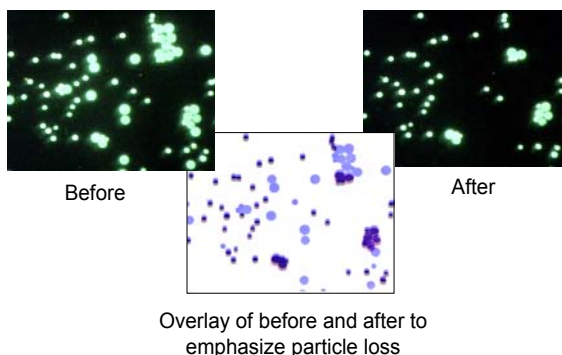
Program: Forensics and Homeland Security

Abstract: The Transportation Security Administration (TSA) is currently evaluating next generation walk-through portal explosive screening devices to support security checkpoint screening at US airports. In a portal detection system, an object or person is subjected to an air jet array that dislodges and transports explosive particles to an ion mobility spectrometer for identification and detection. The ability to remove particles from various surfaces is the critical first step in successful detection of trace explosive residues. In the Surface and Microanalysis Science Division at NIST, we are developing the methodology to determine particle removal rates from various surfaces likely to be encountered in an airport screening environment.

Purpose: The objective of this work is to help study particle release/collection in portal scanners by studying particle removal rates from various surfaces using directed air jets. We are interested in the conditions necessary to optimize remove of particles of various sizes and compositions.

Major Accomplishments: We have assembled a system to test gas jet removal of particles from surfaces. With this system, we utilize monodisperse fluorescent polymer spheres ranging from 1 μm to 45 μm in diameter as test particles distributed on two materials; polycarbonate surfaces and muslin cloth. In this initial set of experiments, we are using spherical particles in an effort to verify our experimental approach before studying more complex particles (high explosives) and surfaces. After particles are dispersed on the substrate, optical images of the sample surface are taken with a fluorescence microscope using 488 nm laser illumination. A high velocity, computer controlled, nitrogen gas jet is used to remove the particles from the surface. Micrographs are taken before and after exposure of selected areas of the surface to the gas jet. Particle removal rates from the respective surfaces are determined by particle counting implemented through image processing and analysis. The micrographs shown in Figure 1a illustrate typical before and after images and subsequent identification of the particles removed by the air jet exposure. Figure 1b shows a plot of the particle removal efficiency as a function of jet pressure for particles of different sizes on a polycarbonate surface. Here the measured jet pressure relative to ambient lab room pressure ($P_{\text{jet}}/P_{\text{atm}}$)

Micrograph of 20 μm and 40 μm Fluorescent Spheres on Polycarbonate Before and After Air Jet



is plotted against the percentage loss of particles. The pressure ratio is proportional to the gas velocity (and other fluid dynamic parameters) and for $P_{\text{jet}}/P_{\text{atm}} < \text{ca } 1.8$, the jet is subsonic. The figure demonstrates that the particle removal efficiency is strongly dependent on particle size. Particles in the range of 6 μm -10 μm in diameter and smaller (1 μm particle data not shown) are tightly bound to the surface and are not effectively removed by our pulsed air jet system. Since the size of explosive particles in trace residues (such as fingerprints) appears to be in the

micrometer and smaller range, further optimization of the air jet removal process is needed for effective sampling of these materials.

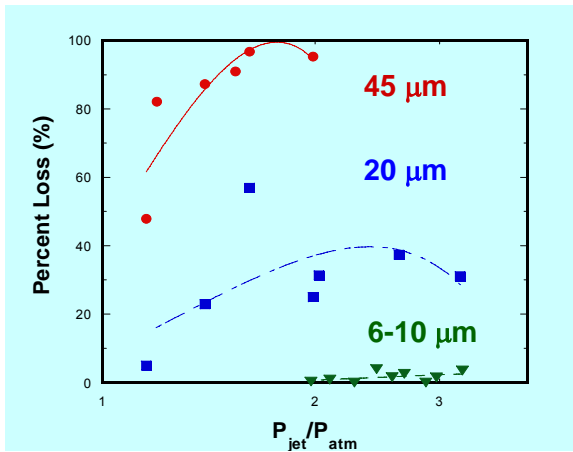


Figure 1a. Fluorescent micrographs of polymer spheres on a polycarbonate substrate before and after gas jet application. An overlay of these two images (inset) demonstrates identification of removed particles (light blue). Figure 1b. Plot of particle loss from polycarbonate filters for 45 μm (circles), 20 μm (squares) and 6 μm – 10 μm polystyrene spheres (triangles) as a function of gas jet pressure relative to ambient pressure. A quadratic fit was made to the data.

Impact: Our work may help improve the design of next-generation explosive detectors by defining optimal parameters for air jet removal of particles. The metrology capabilities that we have implemented will also be used to test new and improved methods for particle removal including the use of ionized air and CO₂ gas jet systems.

Future Plans: After completing our preliminary measurements, we plan to utilize high explosive and drug particles residing on cloth, paper and luggage surfaces. We plan to increase the reliability of the measurement by automating both data acquisition and image analysis.

Refractive index measurements of FBI liquid for forensic glass particles

Authors: J.R. Verkouteren

Program: Forensics and Homeland Security

Abstract: Microscopic glass particles play a major role in forensic analysis aimed at linking individuals to crime scenes. Refractive index can be used to prove a common source of glass particles, and is readily measured from microscopic particles using relatively inexpensive equipment. The FBI uses a light microscope-based heating stage technique for refractive index measurements, and disseminates reference materials and training to hundreds of crime labs throughout the country. The measurement technique requires that the glass particles be immersed in a liquid, the refractive indices of which are known for wavelengths spanning the visible range, and for temperatures ranging from ambient to 100 °C. The FBI requested calibration of their immersion liquid through the Office of Law Enforcement Standards (OLES), and the work was conducted and completed by CSTL. The highly precise technique used by CSTL indicates that the FBI may not be able to achieve the accuracy they need with this particular immersion liquid. A companion project being conducted by the Physics Laboratory at NIST, in conjunction with CSTL, to calibrate a glass standard will provide the means to judge the accuracy of the light microscope technique.

Purpose: Microscopic glass particles are one of the more common pieces of forensic evidence used to link individuals with crime scenes. Refractive index can be a unique characteristic that serves to link glass particles with those at the crime scene, and can be easily measured with relatively inexpensive equipment and thus is a common measurement in crime labs. The success of litigation often hinges on the accuracy of the measurements, and the FBI, which has a responsibility to disseminate training and reference materials to crime labs, requested help through OLES in determining the accuracy of their measurement technique. The FBI uses a light microscope-based heating stage technique for refractive index measurements, which requires a liquid calibrated for refractive index at wavelengths throughout the visible light range and at temperatures from ambient to 100 °C. The FBI uses a specific immersion liquid that they have already disseminated to crime labs, and requested that this particular liquid be calibrated. CSTL has a refractive index measurement technique demonstrated to produce results with uncertainties at the level required by the FBI and therefore OLES requested that CSTL perform the measurements.

Major Accomplishments: The refractive indices of the FBI liquid were measured at 4 wavelengths in the visible and at 3 temperatures ranging from 20 °C to 65 °C using the method of minimum deviation (Figure 1). The data were modeled to provide equations to calculate refractive index at any temperature from 0 °C to 100 °C and at any wavelength in the visible. The uncertainties are an order of magnitude larger than the level requested by the FBI owing to limitations of the liquid itself. The FBI liquid is very viscous and optical homogeneity was compromised, probably as a result of persistent temperature gradients on the order of a few hundredths of a degree C. As the light microscope technique used by the FBI depends on temperature stability of the same order for optimum refractive index accuracy, our results indicate that this liquid is probably not the best choice for a reference liquid.

Impact: Crime labs throughout the country collecting refractive index data on glass particles must know the accuracy of the technique in order to support their results in the courtroom. Our work with the FBI will help to establish the uncertainties of the method by working to establish appropriate reference materials.

Future plans: Our task is completed, although the need for a new immersion liquid is indicated. There is a companion project for next year, led by the Physics Laboratory and involving some CSTL collaboration, to produce a glass standard reference material as a calibration material for the immersion technique. With both a glass SRM and a calibrated liquid, any crime laboratory can determine the uncertainties of the refractive index immersion technique.

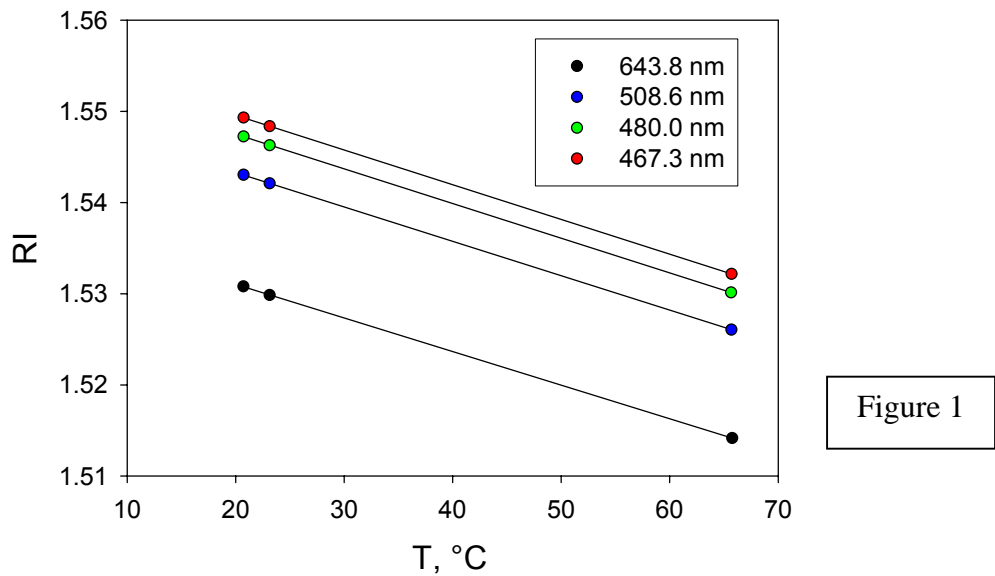


Figure 1. Plot of the refractive indices of the FBI immersion liquid provided to NIST for calibration. The sample was measured at 4 wavelengths in the visible and at 3 temperatures ranging from 20 °C to 65 °C using the method of minimum deviation.

Molecular Electronics Metrology

J. D. Batteas,* J.C. Garno,* C.A. Gonzalez[†], C.A. Hacker,[□] L.J. Richter,* S. W. Robey,* C. D. Zangmeister,[‡] and R. D. van Zee[‡] ([□]Div 812 [‡]Div 836, *Div 837, [†]Div 838)

Program: Technologies for Future Measurements & Standards

Scientific Objectives. Molecular Electronics (“moletronics”) is a field that many predict will have important technological impacts on the computational and communication systems of the future. In these systems, molecules perform the functions of electronic components. Our objectives are to characterize the structural properties of, and the conduction mechanisms through, molecules and to develop methods that reliably and reproducibly measure the electrical properties of molecular ensembles in test structures.

The drive to increase electronic device performance, with the associated push to ever smaller device dimensions, has lead industry observers to conclude that silicon-based technology will reach a point of diminishing gains in the near future. This, in turn, has generated interest in alternative technologies based, for instance, on single-electron devices and molecular components. It is hoped that the tremendous flexibility available with organic synthetic chemistry and self-assembly techniques can be harnessed to produce non-linear devices analogous to silicon-based diodes and transistors, but comprised of single or small numbers of molecules. The CSTL team of researchers in molecular electronics is integrating a range of techniques that will provide key information on electronic structure and electron transport in candidate molecular electronic systems. The experimental approach includes two-photon photoemission, which accesses unoccupied electronic levels and tracks electron relaxation effects, scanned probed microscopies, which can characterize electron transport down to the single molecule level and afford means of manipulating matter on the nanometer scale, and theoretical modeling of electronic states and transport properties to better elucidate the mechanisms involved in electron transport through molecules.

Purpose: This work will develop measurement techniques and expertise necessary to

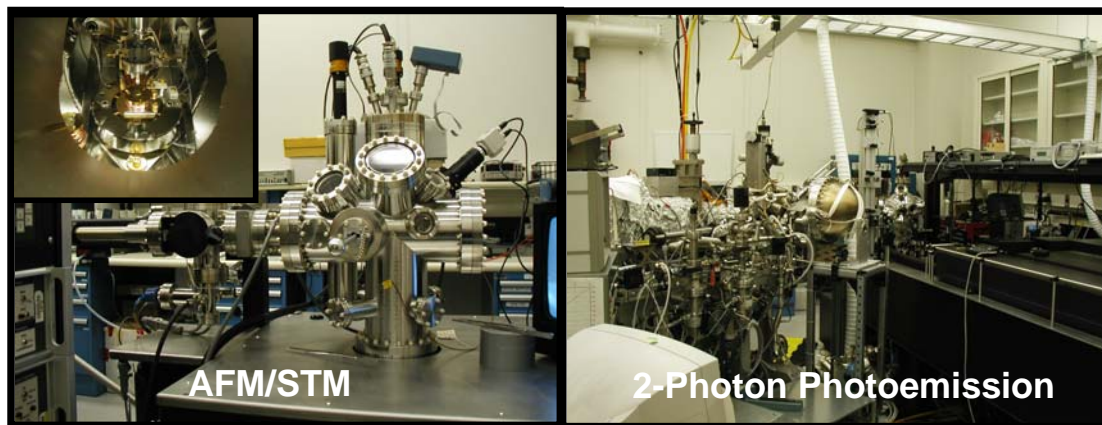


Figure 1. Left, Atomic-Force/Scanned-Tunneling Microscope used for studying electron tunneling in self-assembled monolayers. Right, Ultrafast laser and vacuum system used to in photoemission studies.

understand electronic structure and electron transport through molecular monolayers

and small, molecular ensembles. The overall goal is to reliably provide experimental details which, when coupled with theoretical input, will help to elucidate the physical mechanisms that produce device function in molecular based systems. This work is also aimed at providing the requisite measurement protocols for such systems.

Major Accomplishments: *Theoretical Studies of Electron Transport in Molecular Wires.*

We have continued our study of the possible mechanisms governing electron transport in molecular wires. Particular attention has been focused to the electrostatics at the molecule-metal interface, which has been found to affect significantly the transport properties of the system. In order to properly describe the electrostatics at the interface, a novel algorithm has been developed that efficiently computes the electrostatic potential

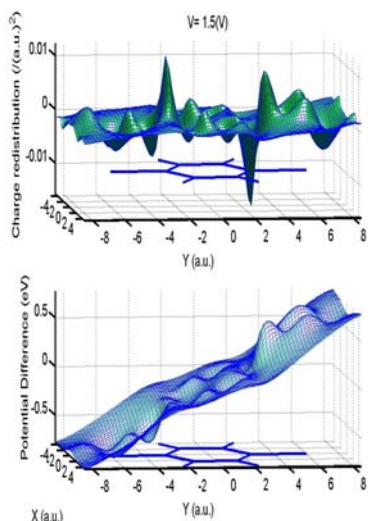


Fig 2. Charge Distribution and Electrostatic Potential profiles for benzene di-thiolate attached to gold electrodes.

by solving the Poisson equation at each cycle of the self-consistent field iteration based on *ab initio* electronic structure calculations. A result of this calculation is shown in Figure 2. This algorithm has been used to study the possible sources that lead to asymmetric current-voltage (I-V) curves in atomic wires as well as in a series of organic thiolates connected to gold electrodes. In order to develop efficient and robust models to gather a qualitative picture of electron conductance through molecular bridges, a simple algorithm to compute the first-order expansion of the system's Green function projected only onto fragments of the isolated molecule (no electrodes are included) has been implemented. This simple model, called the Green Function Condensed-to-Fragments model (GFCF) was found to be very useful in studying electronic transport properties of molecular bridges where the contact to the electrodes does not seem to play an important role in determining the shape of I-V curve. This approach has been used to compute I-V

characteristics of the molecule 2' amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiolate (NH₂-NO₂-OPE), found to exhibit “negative-differential resistance” (NDR) behavior at 60 K. The results of the calculations are in good agreement with the experimental I-V curves. Calculations based on the same model predicted that the fluorinated derivative 4,4'-di(ethynylphenyl)-2'-fluoro-1-benzenethiolate (F-OPE) was also a good candidate for NDR behavior. Chemists in the Nanotechnology Group at Kraft Foods worked on the synthesis of the molecule and very recently, scientists in NIST's Surface and Microanalysis Sciences Division (837), have made I-V measurements that qualitatively agree with the predictions of this model. This is the first time that a theoretical prediction of the behavior of molecular bridges upon electrification has prompted experimental work leading to its validation. These results indicate the potential of theoretical tools in

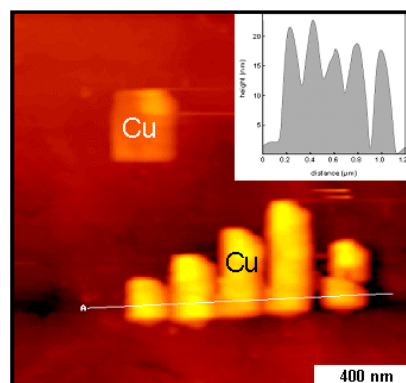


Fig 3. Patterned Cu contacts on the SAM surface. Patterns range from 150 nm to 400 nm and are ≈20 nm thick.

the rational design of electronic devices at the nanometer-scale.

SPM Directed Device Fabrication. Precisely engineered nanostructures provide a means for the exploration of chemical reactions under spatially well-defined and controlled environments. Although not yet practical for high throughput applications and manufacturing, scanning probe lithography studies provide fundamental information on tip-surface interactions, structures, and properties at the level of nanometers. Under the support of ATP, nanometer-sized patterns of copper were constructed at dimensions ranging from 100 nm to 400 nm using a AFM-based lithography (Cf. Figure 3). The writing density and size of the patterns affect copper growth. Varying solution chemistry parameters, such as the immersion intervals and the concentration of metal salts, can control pattern sizes. Copper grows beyond the edges of the pattern boundaries. An effective resist was found using mercaptoundecanol, with very high selectivity observed, even at the nanometer scale. Longer chain length alcohols (C_{11} vs C_6) were more effective as resists. Preliminary results using silanized tip coatings show promise for inhibiting copper deposition on AFM tips during *in situ* experiments. Future work will investigate charge transport with copper overlayers on SAMS using conductive probe AFM measurements at a metal-molecule-metal interface.

Orientational Effects on Electron Tunneling in Dodecanethiol. Obtaining a detailed

understanding of electronic transport properties in molecules requires the ability to correlate structure and transport mechanisms. Here we are utilizing dodecanethiol as a “standard” test molecule to provide reference I-V measurements. This molecule affords a means of probing the impact of molecular orientation on tunneling behavior. Self-assembled monolayers of dodecanethiol have been prepared with regions of densely packed molecules whose molecular axis is oriented $\approx 30^\circ$ from the surface normal right next to regions of lower density molecules which are arranged with the molecular axis parallel to the surface. Asymmetry in the tunneling I-V curves show that, in the case of the standing up phase, the tunneling behavior is rectified by the asymmetry of the transport junctions, while in the laying down molecule, this asymmetry is almost completely removed (Cf. Figure 4) and may be explained by differences in metal surface potentials of the tip and sample surface.

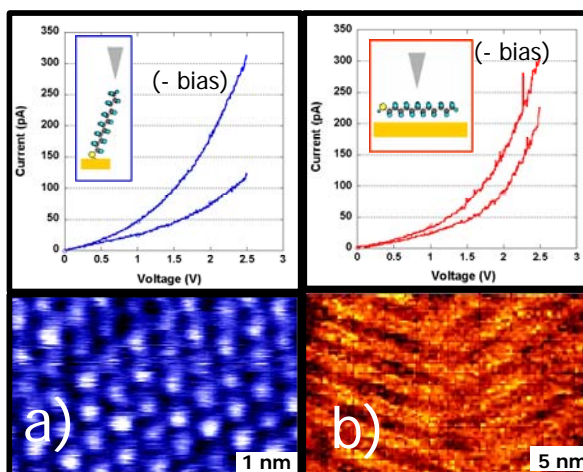


Fig 4. Orientation dependence on tunneling behavior in dodecanethiol showing asymmetric I-V behavior in molecules standing up on the surface (a) vs. more symmetric behavior in molecules laying down (b).

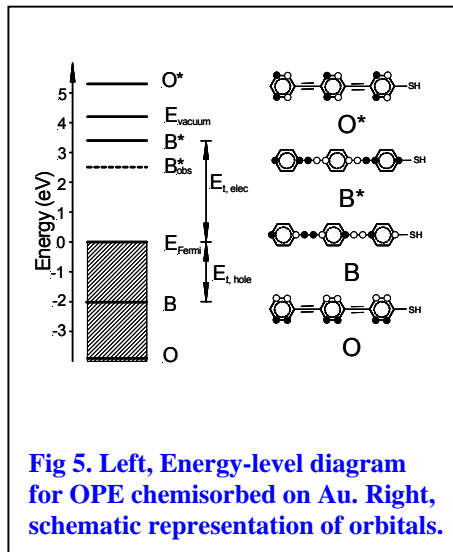
Spectroscopic Measurements. The geometrical configuration and the electronic structure of electrically-active molecules are believed to be governing factors in molecular conductance. To investigate whether these molecular properties are related to the test-structure measurements, ultrafast laser spectroscopies have been used to study the

geometry and electronic structure of molecular films. The electronic structure of these films was studied using one- and two-photon photoemission.

Specifically, oligo(para-phenylene-ethynylene) thiolate chemisorbed on gold surfaces was studied. Within 5 eV of the Fermi level, four states were observed, two occupied (2.0 eV and 4.0 eV below the Fermi level, designated B and O in Figure 5) and two unoccupied (3.4 eV and 5.3 eV above the Fermi level, B* and O*). This information is shown in the energy level diagram. The two states closest to the Fermi level are assigned to pi-conjugated molecular orbitals along the backbone of the molecule, and the other two are assigned to molecular orbitals formed by the "ortho" carbons. (See schematic representation of these orbitals in Figure 5.) From this assignment, the hole- and electron-barriers can be determined. These are, respectively, 2.0 eV and 3.4 eV, using a transition-maximum criterion. The charge transport gap can also be estimated. It is between 3.8 eV and 5.4 eV, depending on the criterion used to determine the onset of transport.

Impact: This project is providing detailed insight into the complex behavior of electronic transport through molecules. The program combines for the first time detailed theory and molecular scale measurements that can provide a basis for the complete understanding of electronic structure and transport effects in molecular electronic systems. The foundation that these results provide not only benefits the development of molecular electronics applications, but also affords a groundwork for the investigation of molecular based optoelectronic device applications.

Future Plans: On the horizon are experiments aimed at probing the electrical behavior of ensembles of molecules based on patterning to afford a means of assessing molecular function in device level measurements, as well as scaling conductance properties in molecular ensembles. Future work will be aimed at correlating compression effects on the tunneling properties as investigated by conducting probe atomic force microscopy. The results from these experiments will be compared to theoretical models and to the performance of device-prototypes fabricated and tested by our collaborators in NIST's Semiconductor Electronics Division (812). The photoemission work will systematically investigate the effects of chemical substitution on the molecular orbitals. Theoretical modeling of the transport properties and the valence structure of these electrically-active compounds is also underway.



Growth of Oriented ZnO Nanowires on Sapphire and Gallium Nitride

Babak Nikoobakht and Stephan J. Stranick

Program: Technology for Future Measurements and Standards

Abstract: One of the main goals of this work is to develop novel methods to grow and manipulate semiconductor nanowires. These nanowires have unique properties that make them well suited for applications in opto-electronics and as potential building blocks of future measurement platforms. To this end, we have begun to detail the process conditions that determine the orientation and morphology of ZnO nanowires; successfully generated patterned arrays of semiconductor nanowires, nanodots, and extended nano-systems; and have now begun to elucidate the key aspects of the growth mechanism. In continuation of this work, these methodologies will be further refined and then employed to generate novel opto-electronic devices for use in sensor and proximal probe applications.

Purpose: We have set out to develop novel methods to grow and manipulate semiconductor nanowire. These nanowires have unique properties that make them well suited for applications in opto-electronics and as potential building blocks of future measurement platforms. For example, nano-light sources and detectors can be realized by engineering a nanowire with a diode junction/functionality. This along with other nano-device functionality could enable the development of sensor arrays capable of performing quantitative chemical measurements.

Major Accomplishments: ZnO nanowires (NWs) are grown on sapphire and GaN surfaces via a vapor-phase transport process using Au thin film as catalyst. We have been able to successfully control the growth direction of individual ZnO NWs and the morphology of their ensemble. We present the first examples of vertical and 60°-tilted NWs on c-plane sapphire, vertical NWs on GaN substrate and unidirectional growth of horizontal NWs on a-plane sapphire. In the case of normal NWs on sapphire and GaN, XRD analysis shows that single-crystal *wurtzite* NWs grow in the [0001] direction normal to the basal c-plane, which proves that a-plane sapphire is not essential for growth of vertical ZnO NWs. We have found that the thickness of the Au-film and pre-growth annealing of Au/sapphire substrate are critical in controlling the morphology of the nanowires. Utilizing the above factors, two new morphologies have been selectively synthesized. AFM and SEM studies show that in the absence of annealing, Au films with feature heights between 1 to 10 nm result in NWs 60° tilted with respect to the surface, whereas pre-annealed Au films with heights below ~6 nm result in growth of NWs in the surface normal direction. For the annealed Au films thicker than 6 ± 2 nm, a network of ZnO is formed followed by the growth of NWs in the surface normal direction. We have attributed the normal and tilted growth directions to the surface concentration of O and Al ions on sapphire. In order to form horizontal NWs, results show that the

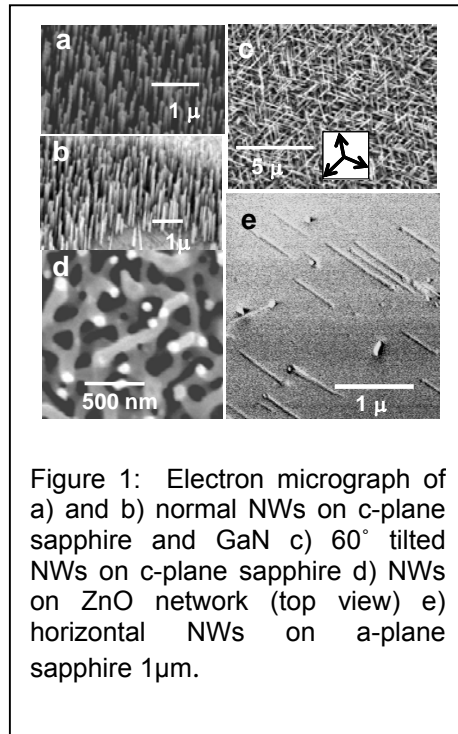


Figure 1: Electron micrograph of a) and b) normal NWs on c-plane sapphire and GaN c) 60° tilted NWs on c-plane sapphire d) NWs on ZnO network (top view) e) horizontal NWs on a-plane sapphire 1μm.

substrate needs to be a-plane and instead of an Au film as catalyst, scattered Au droplets with diameter less than 15 nm must be present on the surface. In this case NWs all grow in (110) direction on the basal plane of the a-plane sapphire.

Impact: Nanowire devices will provide multiple options as building blocks for sensors, miniaturized measurement platforms, and as advanced scatter probe structures, enabling true nanometer spectroscopy. This methodology will provide an inexpensive and straightforward approach to the synthesis of sensing devices with multiple functionalities that can be integrated to form state-of-the-art measurement systems. The findings of this study have been submitted for publication in *Advanced Materials* and *Journal of Physical Chemistry B*.

Future Plans: Our preliminary studies have focused on the growth and manipulation of semiconductor nanowire. These methodologies will be further refined and then employed to generate novel opto-electronic devices for use in sensor and proximal probe applications.

Electron Probe Characterization of KNbO₃ and NaNbO₃ Single Crystals for use as Quantitative Microanalysis Reference Materials

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 *"Jožef Stefan" Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

CSTL Program: Microelectronics

Abstract: Potassium and sodium niobate single crystals were evaluated with the electron probe microanalysis (EPMA) using wavelength dispersive spectrometers (WDS). Alkali metal migration that usually occurs in materials exposed to the electron beam, was minimal or non-existent. The microheterogeneity determined from line traverses and random points was minimal with all analysis points being less than the expanded 3 σ uncertainty predicted from the x-ray counting statistics for each element. Quantitative analysis was also in agreement with the expected stoichiometry of the crystals although a Ca impurity of 0.3 % mass fraction was found in the NaNbO₃ specimen.

Purpose: Reference standards are needed for EPMA of alkali niobates with the general formula K_{1-x}Na_xNbO₃, a ferroelectric material with perovskite structure. The ceramic material K_{0.5}Na_{0.5}NbO₃ (KNN), a solid solution of the two alkali niobates, is of major interest because of its high piezoelectric coefficients and moderate dielectric permittivity. Complicated fabrication can lead undesirable multiphase ceramics; therefore, a careful characterization of the product is required on the μ m scale to verify that the desired composition has been produced.

Major Accomplishments: Stability of all elements in both crystals was verified using a point electron beam at currents of 20, 50, and 100 nA, at each of two or three excitation potentials, 10 keV, 15eV, and 20 keV. Five 20-s consecutive measurements were made on each point. Plots of counts versus time for all points were linear for all elements demonstrating that no migration of the alkali metals occurred. For heterogeneity testing of all elements 40 point-beam traverses across the two specimens were made with 2 μ m steps at 15 keV, 50 nA, and 20-s counting times. Plots of element x-ray counts vs. distance showed that all points for a single trace of a given element in a specimen fell within the limit of the expanded uncertainty (3 σ) for N, the average number of counts. This and additional random-point data from both specimens confirm the microhomogeneity of these crystals. Results of quantitative analysis of the crystals at 15 keV and 50 nA using Nb, Nb₂O₅, NaAlSi₃O₈, KAlSi₃O₈, and CaTiO₃ standards are in the

	% Mass Fraction (1 σ uncertainty in parentheses)					
	KNbO ₃			NaNbO ₃ (0.30 % mf Ca)		
	K	Nb	O (stoic.)	Na	Nb	O (stoic)
EPMA-WDS	21.56 (0.14)	51.54 (0.16)	26.90	14.08 (0.08)	56.53 (0.20)	29.09
Nominal	21.72	51.61	26.67	14.03	56.69	29.28
KNN Anal.	9.97 (0.28)	19.98 (0.31)	60.31 (0.41)	9.74 (0.26)	Form. K _{0.50} Na _{0.49} Nb _{1.00} O ₃	

table below. Also included in the table is the quantitative analysis of the KNN specimen using the niobate crystals as standards.

Impact: The KNbO_3 and NaNbO_3 single crystals tested appear to be excellent reference materials for characterizing KNN ceramics with EPMA on the μm scale. In addition, because no migration of the alkali elements were observed when these specimens were tested with a high-energy electron beam, these materials will make excellent K and Na reference standards for the microanalysis of other alkali-containing materials.

Future Plans: We would like to obtain more of these single crystals, hopefully enough to be able to more extensively characterize sufficient material for distribution as Interactive Materials (IMs) or, even better, as NIST SRMs. They will be very useful to the microanalysis and ceramics communities.

Development Of Sem-Eds Analysis Procedures For C, N And O To Enable Characterization Of Explosives Particles, Polymeric And Organic Materials

J.T. Armstrong and J.A. Small

Program: Forensics and Homeland Security AND Exploratory Research

Abstract: Procedures were developed for quantitative phase identification of organic particles and surface layers using energy dispersive x-ray analysis (EDS) in a scanning electron microscope (SEM) to determine C, N, and O relative concentrations as well as those of heavier elements. Tests of these procedures on gunpowder grains and explosives microparticles showed that, although radiation damage induces partial dehydration in these materials, repeatable steady-state residual compositions are left that can be used for accurate phase identification.

Purpose: We explored the degree to which elemental analyses including C, N and O (using modern thin window energy dispersive x-ray detectors) can be utilized in current generation scanning electron microscopes to accurately characterize organic materials, hydrated species, and oxy-anion phases. We then used the procedures we developed to determine the degree to which SEM/EDS analysis can be made into a more effective tool for identification of organic microparticles, such as gunpowder and explosives particles, polymers and organic contaminants.

Major accomplishments: Using several commercial thin window EDS analyzers, we found that C, N, and O can be routinely measured with detection limits of better than 0.5% for C and O and ~1% for N in the presence of major C. Measurement precisions of ~0.5% (absolute) can be attained for these elements. Although some commercial software packages were found to fail in attempts to separate peaks from backgrounds for these elements, sequential simplex in NIST's DTSA program was found to work satisfactorily. Optimum correction procedures for these elements were identified and tested on standard (inorganic) multilayer specimens (insulating organic particles need to be coated with a conducting material, we chose Au). Results showed comparable accuracy to that obtained for elements like Na, Mg, Ga, Ge, and As (commonly analyzed elements having low energy x-ray lines). The major problem found in analyzing organic materials was, as expected, radiation damage and decomposition under electron bombardment. Procedures were tested that minimized this damage, but none were found so far that completely eliminate it. We found, however, that the degree of decomposition during analysis could be controlled, resulting in repeatable, distinctive residue compositions – even for materials as volatile as RDX explosive (RDX decomposes from $C_{20}N_{15}O_5H_x$ □ $C_{20}N_{10}O_3H_x$ □ $C_{20}N_6OH_x$, gunpowder from $C_{20}N_5O_{15}H_x$ □ $C_{20}N_5O_5H_x$ □ $C_{20}N_4O_2H_x$). The data suggest that by use of controlled conditions, “fingerprint” C-N-O EDS spectra can be obtained from analysis of organic particles and thin layers that could be used to identify their initial phase composition. See figures 1 and 2.

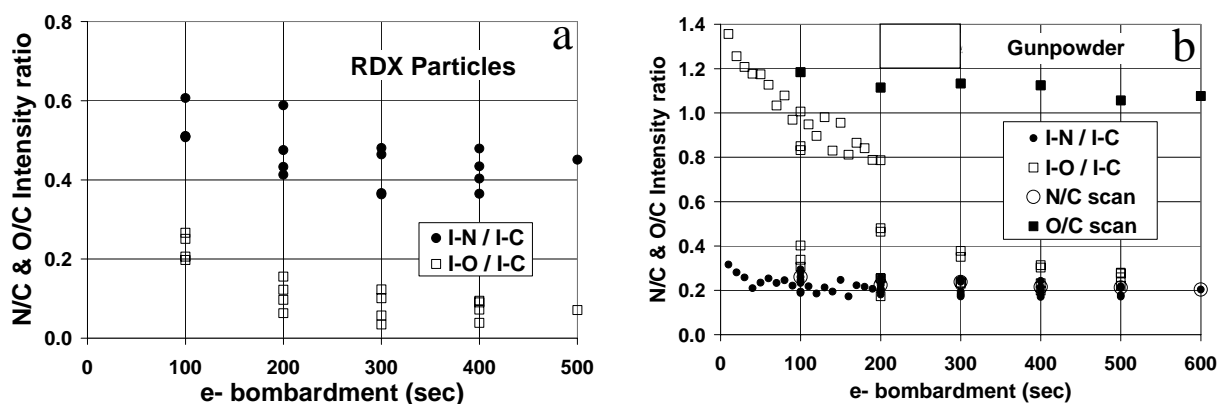


Fig. 1. Decrease in relative intensities of nitrogen and oxygen with respect to carbon as a function of electron bombardment time for RDX (a) and gunpowder (b). Trends are determined by a series of replicate analyses in the same spot. In both materials, a distinctive steady state composition of residual C-N-O is eventually obtained.

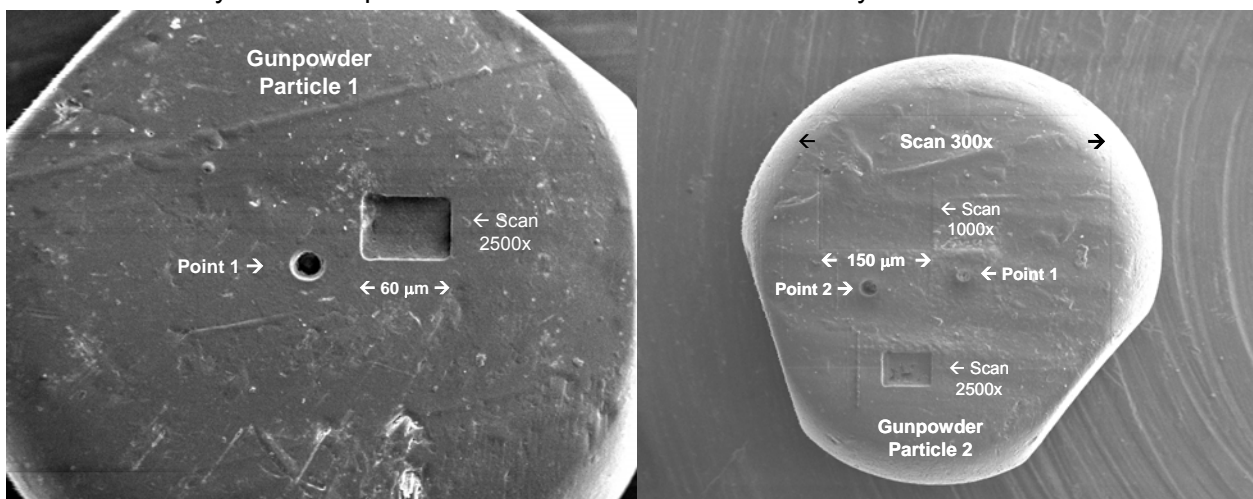


Fig. 2. SEM images of gunpowder particles whose analytical results are shown in Fig. 1b. Note visible radiation damage inflicted by the electron beam during analysis. As expected, damage is less when the beam is rastered than when it is focused. Minimal damage is seen for the 'whole particle' 300x scan in Fig. 2b; however, even here significant oxygen loss occurred (Fig. 1b).

Impact: Accurate EDS analysis or phase fingerprinting of C, N, and O will open a vast potential range of applications for analytical scanning electron microscopy that could potentially double its usage or more in areas as important and disparate as forensics and homeland security, nanotechnology, microelectronics, pharmaceutical analysis, corrosion research, failure analysis, and environmental sample analysis.

Future plans: This work completed a one-year feasibility study conducted as an exploratory research project. The results are promising enough to warrant future work. If this area is tasked for future research, we propose ramping up this project to develop experience with a wider range of organic materials and a wider range of beam dose conditions. When the liquid nitrogen cold stage is delivered and installed on our Auger microprobe (with EDS capabilities), we propose testing whether cryoanalysis would

significantly improve sample stability measurement reproducibility. We propose to continue our study to provide improved methods of background subtraction that could be incorporated in commercial EDS software. We plan to publish the methods explored in this study once they have been refined and demonstrated to be robust over a wider range of materials and analytical conditions. We plan to publish a report of the accuracy of existing correction procedures for C-N-O quantitative analysis in low average atomic number materials – and propose new correction procedure optimization.

Automated Analysis of Organic Particles using Cluster SIMS

Greg Gillen (Div. 837)

Program: Chemical Instrumentation- HTS

Abstract: Cluster primary ion bombardment combined with secondary ion imaging was used on an ion microscope secondary ion mass spectrometer for the high throughput and spatially resolved analysis of organic particles on various surfaces. Compared to the use of monoatomic primary ion beam bombardment, the use of a cluster primary ion beam (SF_5^+ or C_8^-) provides significant improvement in molecular ion yields and a reduction in beam-induced degradation of the analyte molecules. These characteristics of cluster bombardment, combined with automated sample stage control and custom image analysis software, were utilized to rapidly characterize the spatial distribution of trace explosive and narcotic particles on a variety of surfaces.

Purpose: Trace analysis of explosive and narcotic residues is important for homeland security, customs, forensic, law enforcement, and environmental applications. Key issues of research for these applications include the nature of the trace residues to be sampled (particle size distribution of explosives/narcotics in fingerprints, for example), the efficiency of various types of particle collection systems, and the development and characterization of organic particle standard reference materials. Each of the areas requires the use of analytical techniques that can rapidly and uniquely identify micrometer-sized explosive/narcotic particles among a background of ambient particles. We are evaluating secondary ion mass spectrometry (SIMS) for this application. Automated imaging analysis of organic particles by SIMS has not previously been feasible due to the sensitivity limitations imposed by low molecular secondary ion yields, degradation of the sample by the primary ion beam and the prohibitively long acquisition times that are required to survey multiple fields using low primary dose SIMS conditions. However, recent research suggests that the use Cluster SIMS, which provides large enhancements in molecular ion yield and a reduction in beam-induced damage may overcome the previously mentioned limitations, making organic particle searching feasible. In the present study, we explore the uses of SIMS particle searching, combined with energetic cluster ion bombardment using SF_5^+ or C_8^- primary ions, to rapidly characterize the distribution of explosive and narcotic particles on various surfaces to support continued development of trace detection screening technologies for homeland security.

Major accomplishments: Characteristic SIMS mass spectra were obtained from particles (a few micrometers in diameter) of various pure explosives and narcotics dispersed on silicon wafers using either SF_5^+ or C_x^- ($x=1-10$) primary ion bombardment. As expected, cluster bombardment provided large enhancements in molecular secondary ion signals compared to monoatomic bombardment under identical conditions. For example, C_8^- bombardment gave characteristic molecular ion signals for explosives that were 300-1000 times greater than for C_1^- bombardment under identical conditions. All of the samples examined also exhibited significant reductions in beam-induced damage under cluster bombardment. The combination of high secondary ion yields and reduction in beam-induced damage allows us to image the distribution of organic particles while achieving high count rates and short acquisition times. Figure 1 shows the results of an organic particle searching analysis used to identify and size acetaminophen particles in a human fingerprint. This figure shows a mosaic of 100 ion microscope SIMS images displayed as an array of 10 x 10 individual images acquired

using automated control of the sample stage with SF_5^+ bombardment and detection of the $(\text{M}+\text{H})^+$ molecular ion at $m/z = 152$. The histogram in Figure 1 shows the distribution in apparent particle diameter (assuming a circular particle) obtained from image analysis of the particle search data. The inset image shows the individual particles identified in a single field-of-view. SIMS particle searching is currently being successfully employed in our laboratory to determine the distribution of explosive particles in fingerprints, the efficiency of different types of explosive particle collection filters and to study the release of particles during the sampling process.

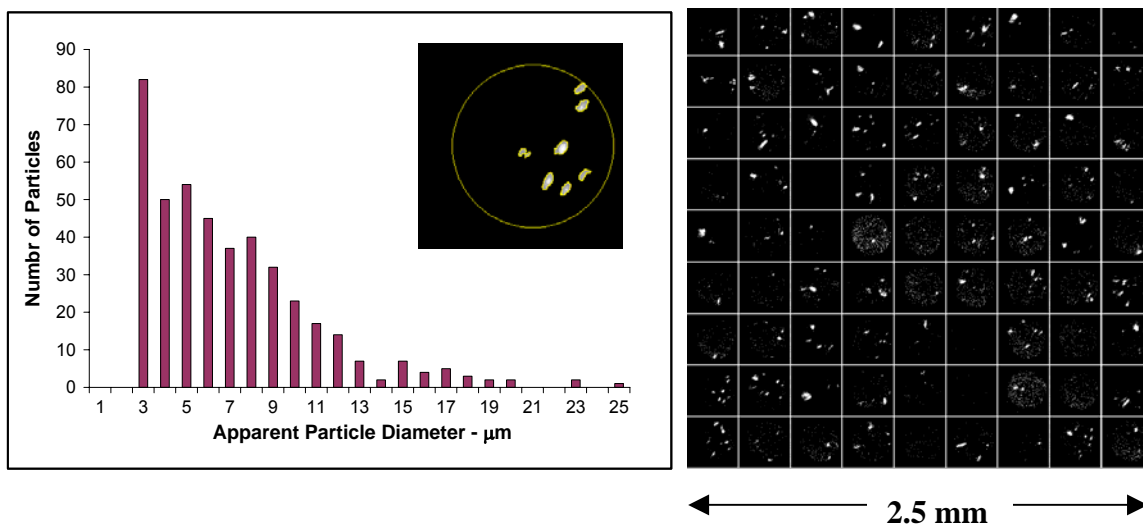


Figure 1: Mosaic of 100 secondary ion microscope images of acetaminophen ($m/z = 152$). Field-of-view for each image is $250 \mu\text{m}$. Image acquisition time 20 s. SF_5^+ primary ion bombardment with beam dose during acquisition of 2.3×10^{13} ions/cm². Histogram on the left shows the calculated size distribution of the particles obtained from the images. Inset shows particles identified in an individual $250 \mu\text{m}$ field-of-view.

Impact: For the high explosives and narcotic compounds examined in this work, cluster bombardment SIMS offers increased secondary ion signals and the capability for minimizing beam-induced damage. These advantages, combined with spatially resolved imaging, allow for the rapid characterization of organic particles on surfaces. This capability is of particular interest for homeland security applications.

Future Plans: We are also working to produce standards for high explosive detection that can be printed onto a variety of different surfaces types (cloth, metal, plastic, luggage) using inkjet printer technology. Development of these materials requires the ability to characterize the quality of the array and an understanding of the interaction of explosive droplets with various surfaces. The automated particle analysis procedure should be ideal for this task.

Particle size characteristics of trace high explosives: PETN and RDX

J.R. Verkouteren

Program: Forensics and Homeland Security

Abstract: Detection of traces of high explosives at screening areas such as airports can be dependent on the collection of particles, particularly for the low vapor pressure explosives RDX and PETN. Particle collection can be accomplished by many methods, including swiping of surfaces, agitation with air jets, etc. Of fundamental importance in determining the effectiveness of any particle collection scheme is the size and distribution of particles expected in the traces left by handling explosives. As the explosive compound is handled, the crystals of the explosive will fragment, and fragmentation is a process that usually gives rise to a power law particle size distribution. The ability to model particle size in explosive traces was tested by measuring the particle size distributions produced by fragmentation of crystals of RDX and PETN. These particle size distributions were found to deviate from a power law, probably due to a tendency of the explosives, particularly PETN, to smear rather than fragment. The data indicate that more small particles are expected to result from fragmentation of RDX compared to PETN, which matches observations of particle sizes in fingerprints produced from C-4 (a compound containing RDX) and Semtex-A (a compound containing PETN).

Purpose: The need to screen for explosives at airports and other points of entry has resulted in the deployment of thousands of trace explosives detectors and created a critical need for effective calibration of these detectors. The detection of traces of high explosives is often dependent on collection of explosive particles, particularly for low vapor pressure explosives such as RDX and PETN. Of fundamental importance in determining the effectiveness of any particle collection scheme is the size and distribution of particles expected in the traces left by handling explosives. Working in collaboration with the Transportation Security Administration (TSA), the NIST Office of Law Enforcement Standards (OLEs), and the NIST Advanced Technology Program (ATP), we are investigating particle size in explosive traces to develop effective methods and materials for testing and calibrating trace explosives detectors.

Major Accomplishments:

To simulate the particle size produced during handling of explosive compounds, crystals of RDX and PETN were removed from the explosive compounds C-4 and Semtex-A, respectively, and crushed to produce populations of particles that were sized using image analysis and scanning electron microscopy. In addition, fingerprints of the two compounds were simulated by handling C-4 and Semtex-A and successively impressing a finger on a series of glass slides for analysis by polarized light microscopy (PLM). The particle size distributions of RDX and PETN deviate from the expected power law (linear under a log transformation) resulting from a fragmentation process (Figure 1), probably due to the tendency of the explosives, particularly PETN, to smear rather than crush. The deviation is more pronounced for PETN, with fewer numbers of smaller particles expected than for RDX. These data agree with PLM observation of the fingerprints, as more small particles of RDX are observed, compared with PETN, although the RDX particles tend to be bound by the plastic matrix. Tenth generation fingerprints of Semtex-A contain many wide (up to 100 μm diameter) thin plates of PETN, consistent with a smearing process.

Impact: Working with TSA, OLES, ATP, and with first responder organizations, our results will be applied to the development of test materials and methods used to determine the effectiveness of trace explosive detectors. Knowledge of the particle size of explosives in trace residues, particularly as they differ for different compounds, will guide the development of challenge samples and sampling schemes. The ultimate goal is to improve detection of explosives residues and therefore support Homeland Security efforts.

Future Plans: The results obtained from this work will be used to guide improvements in explosive particle sampling procedures for trace explosive detection equipment.

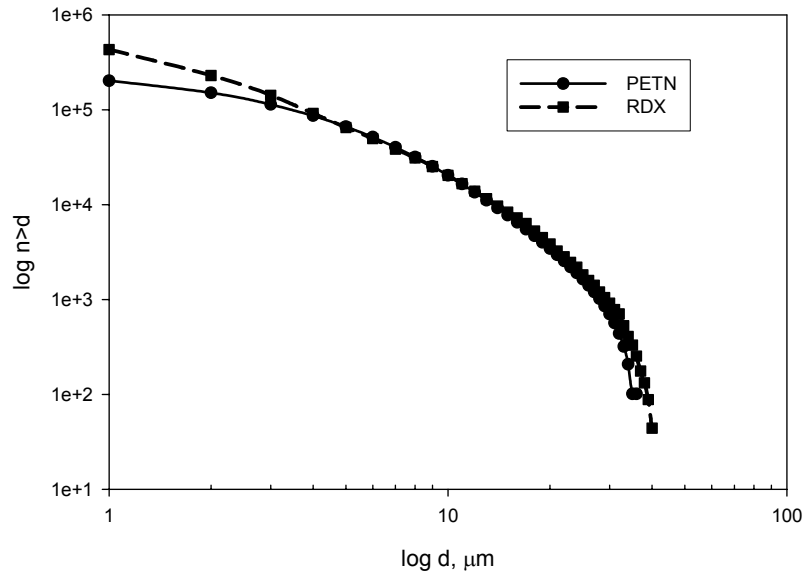


Figure 1. Plot of the particle size distributions of RDX and PETN particles determined by scanning electron microscopy.

Characterization and Control of Gel-Fluid Phase Transitions in Supported Phospholipid Monolayer Films

L.J. Richter (837), C.S.-C. Yang (844), J.C. Stephenson (844) and K.A. Briggman (844)

Abstract Hydrated supported phospholipid structures (Langmuir-Blodgett films, supported bilayers, etc.) have been widely studied as model systems for biological membranes. Supported monolayers and bilayers may also be used as platforms for novel biosensors and biomaterials. The physical structure (gel or fluid phase) of lipid domains in membranes influences cellular signaling and other biological function, and hence must be characterized for both model and biological systems. Until now, it has been difficult to characterize the thermal phase of supported films. We have developed the optical technique of vibrationally resonant sum frequency generation to probe thermal phase transitions of fully hydrated hybrid bilayer membranes. Using this method, we discovered that the gel-fluid phase transition temperatures of the lipid layer in supported hybrid bilayers for a series of saturated phospholipids are ~ 10 °C higher than those in corresponding vesicles. The gel-fluid phase transition can be controlled by selective modification of the hybrid bilayer support. Optical characterization of the lipid phase, combined with chemical control of the phase transition, should enable unique studies of the influence of lipid structure on membrane protein structure and function.

Purpose All cells are surrounded by plasma membranes based on lipid bilayers. Supported lipid bilayer membranes and hybrid bilayer membranes (HBMs) have received considerable interest as they represent simple model systems for the study of cell membranes, and may have technological applications in tissue engineering and biosensors. There is increasing evidence that the physical structure of the lipid membrane has important physiological implications. Lipid microdomains consisting of high phase transition temperature lipids and cholesterol have been implicated in the function of signaling proteins. Conventional calorimetry cannot be done on planar model systems, due to the low surface area. Thus, very little is known of the thermal phase behavior of lipids in supported structures. We are validating optical techniques for the characterization of the thermal phase of supported lipid constructs.

Major Accomplishments Vibrationally-resonant sum frequency generation (VR-SFG) is a non-linear optical probe uniquely suited for the *in-situ* characterization of planar interfaces, as the signal is symmetry forbidden in centrosymmetric media. This selection rule also makes VR-SFG ideally suited to the study of the gel-fluid phase transition in phospholipids, as the methylene CH stretch spectral features in the gel phase are forbidden by the all-trans symmetry of the alkane chains, while these features are allowed in the disordered chain fluid phase. Shown in Fig. 1 is the typical structure of a HBM: a lipid monolayer formed on a hydrophobic film on a solid substrate. Independent control over both the lipid layer and the hydrophobic film may be used to optimize the HBM for specific applications. Shown in Fig. 2 are VR-SFG spectra of HBMs formed with two different phospholipids: Dipalmitoyl-sn-glycero-3-phosphocholine (DPPC) and Dimyristoyl-sn-glycero-3-phosphocholine (DMPC), with 14 and 12 methylene groups per alkane chain, respectively. The lipid chains were perdeuterated to provide contrast against the protonated support. Fig. 2A gives the ratio of the thermal phase dependent methylene CD stretch feature to an internal standard, the CD stretch signal from the terminal methyl groups, for the phospholipids on a well ordered octadecanethiol (ODT) on gold support. The inflection in the step-like increase in the ratio indicates the temperature of the gel-fluid phase transition T_M in the two films. As expected, the longer chain DPPC has a higher T_M than the shorter DMPC

The T_M of HBMs formed on the ODT support is uniformly shifted by $\sim 10^\circ\text{C}$ to higher temperature from the T_M of vesicles (see Fig. 2A). This perturbation of T_M is also observed for HBMs on a support formed from a well-ordered thiolated lipid (TL) film of Dipalmitoyl-sn-glycero-3-phospho-thioethanol. It was discovered that T_M can be controlled by selectively incorporating a small hydrophilic molecule, mercaptohexanol (MCH), into the TL film, introducing slight structural disorder and weak polar forces. HBMs formed on supports fabricated with a 1:2 mole ratio of MCH to TL in the film-forming solution have T_M essentially identical to that of vesicles (see Fig. 2B).

Impact VR-SFG has been established as a diagnostic for the thermal phase of supported bilayers. It was discovered that T_M for the most commonly formed HBMs is significantly different from that of bilayers in vesicles. This change in T_M could affect the biomimetic characteristics of HBMs. A procedure for controlling T_M via modification of support was developed.

Future Plans The ability of VR-SFG to characterize the thermal phase of supported lipid films and the ability to control the phase transition via modifications of the support will be used to study the influence of lipid phase on the insertion and structure of small membrane bound proteins and peptides.

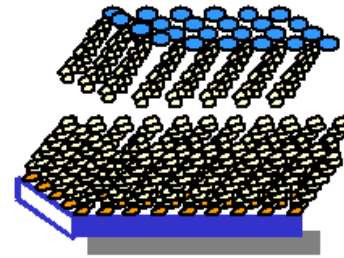


Figure 1. HBM structure

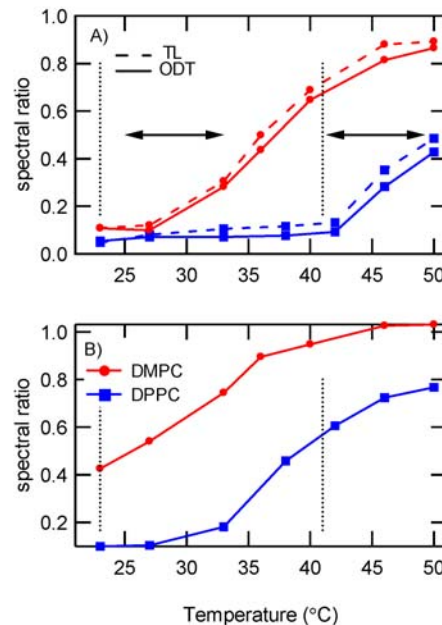


Figure 2. Scaled fluid phase spectral intensity for HBMs formed with **DMPC** and **DPPC**. Vertical Lines mark the T_M for unsupported vesicles. A) HBM support is a pure ODT or TL film. Arrows indicate shift in T_M B) HBM support is mixed TL/MCH film. T_M HBM $\sim T_M$ vesicles.

Development of Phosphorus Ion Implant in Silicon Depth Profile Standard

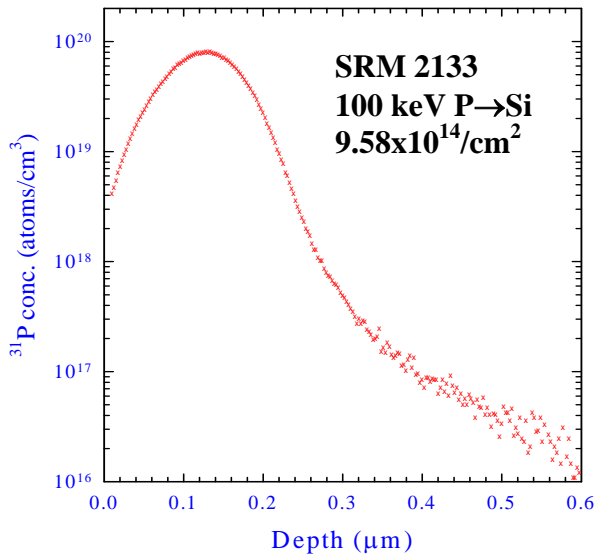
Authors: *D. Simons, R. Paul (Div. 839), W. Guthrie (Div. 898), J. Lu (Div. 898)*

Program: Microelectronics

Abstract: During FY 2003 NIST issued SRM 2133 - Phosphorus Implant in Silicon Depth Profile Standard for calibration of the implanted dose of phosphorus in silicon by secondary ion mass spectrometry, thus completing the suite of SRMs for the major dopant species used in silicon technology. The phosphorus dose was certified by radiochemical neutron activation analysis with an expanded relative uncertainty of 1.7 %. All known sources of uncertainty were considered, including a small spatial heterogeneity among samples. SRM 2133 should meet the needs of the U.S. semiconductor industry for many years based on the projections of the latest edition of the International Technology Roadmap for Semiconductors.

Purpose: The purpose of this work is to provide the U.S. semiconductor industry with a means to measure the implanted dose of phosphorus in silicon with low uncertainty. The shrinking size of microelectronic devices based on silicon technology has led to narrower tolerance requirements for implanted doses of electrically active dopant species, and more attention toward confirmation of electrical models of device performance. Both of these developments require accurate determination of dose values by secondary ion mass spectrometry (SIMS), the analytical method of choice for dopant measurements. Previously NIST had developed and issued Standard Reference Materials for calibration of SIMS measurements of implanted doses of boron (SRM 2137) and arsenic (SRM 2134) in silicon. The specific need for a certified reference material for phosphorus, the third major dopant in silicon, was demonstrated by an interlaboratory round robin exercise that showed nearly a factor of two disparity in measured dose values among participating laboratories when they used their own in-house phosphorus reference materials. That need has now been satisfied through the availability to the U.S. semiconductor industry of SRM 2133 – Phosphorus Implant in Silicon Depth Profile Standard, issued in April, 2003.

Major Accomplishments: The source material for SRM 2133 was a 200 mm diameter silicon wafer that was implanted with ^{31}P atoms at a nominal energy of 100 keV and then diced into 1 cm x 1 cm units with a wafer saw. The total retained dose of ^{31}P atoms was determined by radiochemical neutron activation analysis (RNAA). Aliquots of two independently prepared phosphorus reference solutions were deposited on aluminum foils and served as standards. The resultant certified dose of 9.58×10^{14} atoms/cm² has an expanded relative uncertainty of 1.7 %. All known sources of uncertainty were considered, including (1) measurement replication and heterogeneity for samples, (2) measurement replication for comparator standards, (3) concentrations of standard solutions, (4) radiochemical impurities, (5) volumetric calibrations of standards, and (6) determination of phosphorus carrier yield in the chemical separation. The homogeneity of the phosphorus distribution was tested by fitting the RNAA data from 12 samples to a quadratic model in two dimensions. The uncertainty in the certified value takes into account a small spatial heterogeneity that was detected among samples. A SIMS profile of the depth distribution of phosphorus in SRM 2133 and a picture of the silicon square with its packaging are shown below.



Impact: The relative uncertainty of the certified phosphorus dose value in SRM 2133 should meet the needs of the semiconductor industry for many years, based on the projections of the latest edition of the International Technology Roadmap for Semiconductors.

Future Plans: SRM 2133 completes the suite of SRMs of the major dopant species used in silicon semiconductor technology. At a recent workshop of SIMS users, the greatest interest for new reference materials was expressed for compositional standards of $\text{Si}_x\text{Ge}_{1-x}$, and NIST is presently working to develop such materials.

Materials Evaluation And Database Tabulation For Fundamental Parameters And Algorithms Used For Quantitative Electron Probe Microanalysis

John T. Armstrong

Program: Chemical Instruments – HTS

Abstract: New tabulations of the fundamental physical parameters used in the correction of electron probe microanalysis (EPMA) data have been made and incorporated into the NIST EPMA correction programs (NISTZAF, TRYZAF). Work has continued in making high precision measurements of relative x-ray intensities among well characterized standards as a function of electron beam energy to provide a standard data set that can be used to evaluate these parameters as well as the various correction algorithms employed by the EPMA community. We have begun the formation of an international advisory committee to assist in the evaluation of data for a new NIST website listing evaluated data, parameters, correction algorithms, and a standardized nomenclature for quantitative EPMA that could result in future ASTM and ISO standards.

Purpose: In recent years, much work has been done to better understand the physical processes underlying EPMA and improve the correction procedures employed for quantitative analysis – so much work, in fact, that today literally dozens of different combinations of physical parameters and correction schemes are in use by the active laboratories involved in quantitative EPMA, and are contained in the software packages of the various commercial manufacturers of x-ray analysis instrumentation. A certain carelessness has settled into the EPMA community, in that exactly *which* parameters and algorithms have been employed to calculate elemental concentrations is seldom reported (nor is the raw data typically published). Different implementations of reputedly the same correction procedure can yield significantly different results – either because of errors in the programming or undocumented changes/simplifications in equations and/or parameters. In some commercial systems, the corrections employed in the software are proprietary information and unknown to the user. As a result it has become impossible to directly compare analytical results from different laboratories without adding a significant uncertainty due to the lack of knowledge of how the data has been manipulated. Few laboratories and no current commercial systems make any attempt to quantify the magnitude of this uncertainty in their error budget, although there is abundant evidence that it is often considerably larger than the reported uncertainties in the measurements themselves. This work is part of an ongoing effort to attempt to regularize, standardize and improve the accuracy of EPMA data reduction to be comparable to the level of measurement precision.

Major accomplishments: 1) We have tabulated new sets of the fundamental parameters of use in quantitative EPMA, based on the most recent experimental measurements and theoretical developments, including data extracted from and traceable to the NIST Physics Laboratory Physical Reference Data Base. In many cases these values are significantly different from values currently in common use by the EPMA community. The parameters tabulated and evaluated during the past year and incorporated into the NISTZAF and TRYZAF correction programs include ICRU tabulated mean ionization potentials, the mass absorption coefficients for K-alpha, L-alpha, L-beta, and M-alpha lines between 100 eV and 50 keV derived from the NIST XCOM and NIST FFAST databases, the fluorescence yields compiled most recently by Hubbell, and the new x-ray line and edge energies of Deslattes. These tables are all available in text and spreadsheet files and have evaluative comparisons with previously

used data. 2) We have continued our measurement of relative emitted x-ray intensities as a function of electron beam energy and relative intensities of various x-ray lines among well characterized standards. The multiple beam energy K-line data for pure elements ranging from C to Se in atomic number has been completed and is ready for publication. It has been used to evaluate ionization cross section expressions, Monte Carlo algorithms and some previous sets of experimental measurements. Measurements and studies of the x-ray emission systematics in the systems Cu-Au, Al-Ga-As, and Si-Ge are close to completion with submission for publication anticipated for FY04. The data shows that a number of currently used correction procedures for these elements produce errors of as much as 20% or more. 3) We have demonstrated that accurate correction algorithms exist to predict the variation of x-ray intensity as a function of beam energy. These methods can be used to accurately determine particle and layered specimen compositions (and thickness) without the need to independently standardize at each beam energy used, and can be of assistance in improving the accuracy of the commercially popular "standardless analysis" procedures. 4) We have presented papers this year at the major national and international EPMA meetings proposing institution of a NIST web site to propose developing a standardized nomenclature for EPMA corrections, and a website database listing the standard correction equations and parameters used in the various quantitative EPMA data reduction schemes. This web site would contain the various equations and parameters, the results for test data processed through them, and evaluative data reflecting their accuracy. A number of active researchers in the field have agreed to serve on a committee to evaluate data and propose equations and parameters for inclusion on the site.

Impact: EPMA is potentially one of the most accurate quantitative microanalysis methods – achieving relative accuracies of better than 1% under optimal conditions – and one of the most versatile techniques in terms of the range of analyzed elements and matrix complexity that can be handled without any pre-concentration or other types of specimen alteration. As the technique has matured over the past 50 years, it has become *the* standard method for non-destructive microanalysis in the materials and geological sciences as well as many other fields. The standardization of the correction algorithms (and their corresponding refinement) can result in reduction of uncertainties in interlaboratory data comparison by factors of 2 – 10. The developments in multiple beam energy corrections can greatly improve and increase the application of EPMA to the analysis of surface deposits and layered specimens.

Future plans: This program will continue to ramp up in the coming year. We plan to release the new versions of the NISTZAF and TRYZAF correction programs in FY04, publish the new sets of EPMA parameters on our website, continue evaluation of the various sets of mass absorption coefficients, begin evaluation and tabulation of electron backscatter coefficients and energy distributions, propose a first version of a nomenclature standard, complete and publish standards measurements for the Cu-Au, Al-Ga-As, and Si-Ge systems, continue work on L- and M-line intensity variations with beam energy, evaluate improvement in accuracy of a new atomic number correction that utilizes our new ionization cross section and mean ionization potential data, complete evaluation of the multiple beam energy behavior of insulating vs. conducting materials, and further refine and test correction algorithms with carefully measured standards data.

Progress towards development of an improved method of phase identification by selected area electron diffraction

S. Turner, V.L. Karen, (Material Science and Engineering Laboratory),
D.S. Bright

CSTL Program: Technologies for Future Measurements and Standards

Abstract: Selected area electron diffraction (SAED) is a very useful technique for identification of materials examined by transmission electron microscopy. In combination with chemical information, the structural data obtained by SAED greatly narrows the range of possible phases. SAED has been limited, however, in that information is generally obtained for the sample in only one orientation. Currently, if SAED is obtained for more than one orientation its use is limited because it has been difficult to relate the 3-D information in the diffraction patterns. The recent availability of a double-tilt, rotate sample holder with improved manipulation capabilities along with the availability of reduced cell and phase identification programs developed at NIST suggested the possibility of an improved method of phase identification. Ideally, structural data collected from more than one orientation could be obtained, the geometric relationships determined, reduced unit cells derived and the phase identified from the reduced cells. In this work, the feasibility of this approach was investigated.

Purpose: To explore the possibility of improved phase identification by transmission electron microscopy by applying electron diffraction data obtained from a double-tilt, rotate sample holder to reduced cell and phase matching programs.

Major Accomplishments: In this work, initial steps were made to interface the electron microscope diffraction data from multiple orientations with a reduced cell program for phase identification. Over twenty diffraction patterns and their angular relationships were obtained from a single tetragonal crystal. Diffraction patterns were calculated for the material and a comparison of the calculated and experimental interzone angles showed good agreement. Additionally, diffraction patterns for a cubic material were modeled. Application of the acquired and modeled data to the reduced cell program resulted in unexpected challenges. We have solved some of the problems and can now generate reduced volumes that in some cases are consistent with identification of the analyzed phase.

Example reduced cell determination:

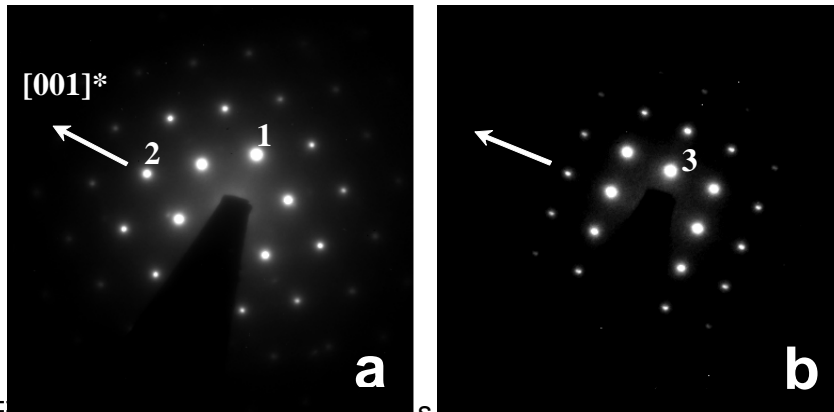


Figure 1. Two diffraction patterns obtained from a rutile crystal rotated around the c axis direction or $[001]^*$ - (a) $[100]$, (b) $[110]$. Three diffraction spots are labeled in the patterns (see text).

The two diffraction patterns in Figure 1 are separated by 45° . Three independent vectors from the two diffraction patterns are chosen (labeled in Fig. 1 as 1, 2 and 3). A unit cell can be formed from these vectors and then a reduced cell determined as summarized in Table 1 (Note: the effect of extinctions are included in the cell measurements).

Table 1. Reduced unit cell derived from two diffraction patterns in Figure 1 and comparison to the rutile unit cell

Vector	Original cell (cm)	Reduced cell (cm)	Reduced cell (Å)	Rutile unit cell (Å)	Parameters
3	7.45	5.25	2.304	4.5929	a
2	8.20	5.268	2.296	4.5929	b
1	5.25	8.20	1.470	2.9591	c
$1 \wedge 2$	90°	90°	90°	90°	α
$1 \wedge 3$	45°	90°	90°	90°	β
$2 \wedge 3$	90°	90.195°	90.195°	90°	γ

After conversion of the reduced cell to d-spacings, calculation of reduced cell volume (7.776 \AA^3) and comparison to the volume of the rutile unit cell (62.421 \AA^3) shows that the reduced cell is a factor of 8.03 smaller than the rutile unit cell. Such determination of reduced cell volumes that are small integer multiples of the phase unit cell volume can be used for phase identification.

Impact: The potential impact of this work, if successful, would be an improved means of phase identification by selected area electron diffraction.

Future Plans: Work will continue on efforts to address problems in the interfacing of multiple diffraction patterns with a reduced cell and the associated phase identification program. More work needs to be done to overcome problems associated with interfacing the experimental data to the programs and to evaluate the effect of uncertainty in the data on phase determination.

Improving limits of detection in microanalysis with high speed energy dispersive x-ray spectrometry (silicon drift detector EDS)

Dale E. Newbury

Program: Technologies for Future Measurements and Standards

Abstract: A critical issue in many applications of electron beam x-ray microanalysis is achieving a low value of the concentration limit of detection, expressed as C_{MMF} (minimum mass fraction). Energy dispersive spectrometers (EDS) typically realize a poorer C_{MMF} than wavelength dispersive spectrometers (WDS) due to poorer resolution and the limited peak counting rate of the EDS. The performance of a new silicon drift detector (SDD) EDS capable of much higher count rates has been evaluated in terms of the C_{MMF} attainable. Trace element constituents (concentration < 0.01 mass fraction) have been detected in less than 10 seconds of spectrum accumulation time.

Purpose: A critical issue in many applications of electron beam x-ray microanalysis is achieving a low value of the concentration limit of detection, expressed as C_{MMF} (minimum mass fraction). The formula for C_{MMF} incorporates with equal weight two critical spectrometry terms, the peak counting rate, P , and the spectral peak-to-background ratio, P/B . The P/B is a direct consequence of the physics of generation of characteristic and continuum (bremsstrahlung) x-rays and the resolution of the spectrometer. For a given target composition and beam energy, the measured P/B is effectively limited by the choice of the spectrometer. Thus, the high resolution wavelength dispersive spectrometer (WDS) provides a better (lower) value of C_{MMF} than the conventional silicon energy dispersive spectrometer (Si-EDS) for equivalent peak counting rates on a particular peak. However, when many trace constituents must be evaluated at each analyzed point, the capability of an energy dispersive spectrometer to simultaneously evaluate the entire excited energy range of x-rays provides a substantial time advantage over the WDS, which must be scanned sequentially over this range with several diffractor changes. In this case, to compensate for the inherently poorer P/B of the EDS, it becomes advantageous to increase the peak counting rate, P . Conventional Si-EDS systems are limited to total spectrum output count rates of approximately 25 kHz.

Major Accomplishments: The silicon drift detector (SDD) energy dispersive x-ray spectrometer, developed by Radiant Detectors LLC of Northridge, CA under NIST SBIR grants, is capable of a much higher counting rate than the conventional Si-EDS. In an SDD, the collection of the charge deposited during photoelectric capture of an x-ray photon is much faster due to (1) a shaped internal electrical field created by a lithographically applied electrode pattern on the back surface; (2) the reduced thickness dimension of the SDD (300 μm compared to 3 mm for Si-EDS); and (3) the higher temperature of operation (250 K vs 77 K for Si-EDS) for faster charge carrier drift velocities. Total spectrum counting rates in excess of 500 kHz have been achieved, limited by the digitization of the data stream not the SDD detector performance.

The SDD can achieve C_{MMF} values of below 10^{-3} mass fraction in short spectrum accumulation times, e.g., 10 s. Figure 1 shows an example of a 10 s spectrum of copper recorded at a total spectrum output count rate of 164 kHz (input count rate \sim 300 kHz). Two examples of trace measurements are shown: the detection of iron at a level of 0.0040 mass fraction, and a C_{MMF} value established for manganese at 0.00092 mass fraction. For a focused beam of 20 keV electrons incident on copper, the total sampled

mass corresponds to 16 picograms of copper. Within this matrix mass, the trace iron constituent corresponds to the detection of 63 femtograms, while the concentration limit of detection for manganese corresponds to 14 femtograms.

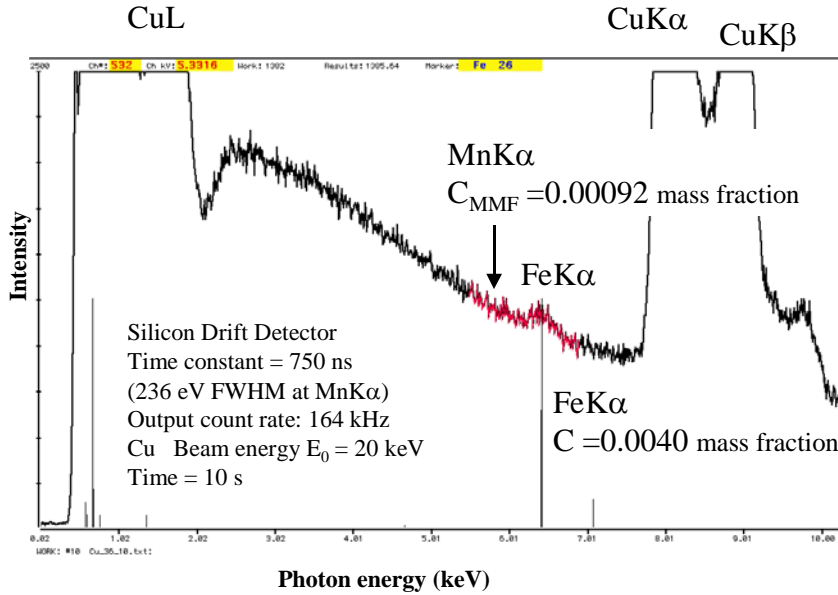


Figure 1. Copper target excited with 20 keV electrons and measured with a Radiant Detectors LLC SDD x-ray detector. The spectral regions for manganese (Mn K-shell) and iron (Fe K-shell) are indicated.

Impact: The conventional monolithic semiconductor EDS device was invented in the U.S. in the 1960s, and U.S. manufacturers dominated the market until the 1980s, when foreign competitors gained a significant market share. The SDD is now emerging as a “killer application” which threatens to sweep away virtually the entire market for conventional monolithic semiconductor EDS devices since the SDD doesn’t require constant liquid nitrogen service and the SDD has been demonstrated to be capable of both higher resolution at long time constant (125 eV for SDD instead of 129 eV at MnK α for Si-EDS) as well as much higher count rates at short time constant (500 kHz to 1 MHz for SDD compared to 25 kHz for monolithic Si-EDS)

Future Plans: An operational SDD detector has been successfully demonstrated in the spectrum acquisition mode to significantly lower the limit of detection in point beam analysis. However, the real promise of the SDD lies in high-speed x-ray mapping. X-ray mapping with the conventional EDS, while widely used, is subject to great time penalties, running to hours, if the analyst wishes to map minor constituents (0.01 to 0.1 mass fraction) or even longer for trace constituents (< 0.01 mass fraction). The SDD has the capability, in principle, to achieve efficient and effective x-ray spectrum imaging, in which an entire x-ray spectrum is saved at each picture element (pixel) of a map with a short dwell time, e.g., 100 ms. X-ray spectrum imaging can greatly improve the utility of mapping by recording comprehensive “flash” maps requiring 10 minutes or less to accumulate but still capable of mapping minor and trace level constituents. The current limitation to this process is the high rate digitization that is required. Existing digital pulse

processing systems become unstable at approximately 200 - 400 kHz when the full spectrum must be sampled with a short integration time (e.g. 10 ms). More research is planned in this area to extend the maximum digitization rate to higher values.

The SDD can have other impacts throughout x-ray spectrometry. A separate SBIR grant to Radiant Detectors LLC has demonstrated that the SDD can serve as the detector for x-rays in a diffractometer, providing distinct advantages over the conventional gas detector by eliminating the need for a monochromator, since the energy resolution of the EDS is sufficient to distinguish the $\text{CuK}\alpha$ and $\text{CuK}\beta$ x-rays from a copper target used to scatter off the crystalline target. A closely related application is the replacement with an SDD of the gas flow proportional counter in a wavelength-dispersive x-ray spectrometer (WDS) used on the electron microprobe. By using the SDD as a high-speed counter, the WDS would become compatible with medium vacuum operation (10^{-6} Pa). The energy resolution of the SDD will also permit easy separation of different photon energies diffracted to the same Bragg angle, $n\lambda = 2d \sin \theta$, where n is the integer order, λ is the x-ray wavelength, d is the crystal plane spacing, and θ is the Bragg angle. When the product $n\lambda$ is the same for two different photon energies, both are recorded at the same diffraction angle. The SDD would show these components as two well-separated peaks.

Development of a New Database for the Simulation of Electron Spectra for Surface Analysis (SESSA)

C. J. Powell; W. S. M. Werner (Contractor); W. Smekal (contractor)

CSTL Programs: Industrial and Analytical Instruments and Services Program

Abstract: A new NIST database has been developed for applications in Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), the two techniques most commonly used for surface analysis. The new database provides data for many parameters needed for the quantitative interpretation of AES and XPS spectra. It also simulates spectra for multi-layered thin-film samples (with layer compositions and thicknesses specified by the user) and measurement conditions specified by the user. The simulated spectra can then be compared with experimental measurements, and the film thicknesses and compositions adjusted to find maximum consistency between the simulated and measured spectra.

Purpose: To provide needed reference data and predictive models for surface analyses by Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) in order to facilitate quantitative interpretations of spectra and improve the accuracy of quantitative analyses.

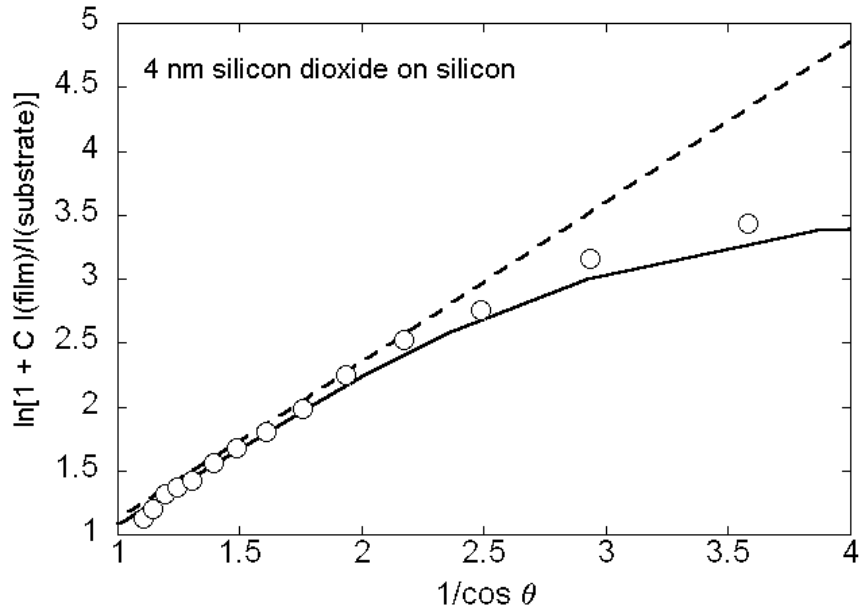
Major Accomplishments in FY2003: A new database, "Simulation of Electron Spectra for Surface Analysis" or SESSA, has been developed for two main applications. First, data are provided for many parameters needed in quantitative AES and XPS:

- differential inverse inelastic mean free paths
- total inelastic mean free paths
- differential elastic-scattering cross sections
- total elastic-scattering cross sections
- transport cross sections
- photoionization cross sections (for XPS)
- photoionization asymmetry parameters (for XPS)
- electron-impact ionization cross sections (for AES)
- photoelectron lineshapes (for XPS)
- Auger-electron lineshapes (for AES)
- fluorescence yields (for AES)
- Auger-electron backscattering factors (for AES)

Second, Auger-electron and photoelectron spectra can be simulated for layered samples. The simulated spectra, for layer compositions and thicknesses specified by the user, can be compared with measured spectra (for conditions specified by the user). The layer compositions and thicknesses can then be adjusted to find maximum consistency between simulated and measured spectra.

The solid line in the Figure shows a plot of a function of the Si 2p photoelectron intensities (I) from SESSA for a 4 nm silicon dioxide film on a silicon substrate as a function of $1/\cos \theta$ where θ is the photoelectron emission angle with respect to the surface normal (the parameter C in the function is the inverse ratio of these intensities for pure samples of SiO_2 and Si, respectively). The open circles show experimental measurements and the dashed line shows the limiting result obtained if elastic scattering of photoelectrons were neglected. The slight differences between the open circles and the solid line for $(1/\cos \theta) > 2$ ($\theta > 60^\circ$) is probably due to variation in the thickness of a

monolayer of carbonaceous contamination that was assumed in the simulation. The difference between the solid and dashed lines indicates the significant effects of elastic scattering of the signal electrons for $\theta > 60^\circ$, as found in previous NIST analytical work.



The Figure shows plots of a function of Si 2p photoelectron intensities (I) for a 4 nm SiO_2 film on a Si substrate as a function of $1/\cos \theta$, where θ is the electron emission angle with respect to the surface normal. The open circles show experimental measurements, the solid line shows results from SESSA, and the dashed line shows the result obtained if elastic scattering is neglected.

Impact: Most quantitative analyses by AES and XPS have been previously based on the implicit assumption that the specimen is homogeneous over the sampling depth for the measurements or that the sample morphology is limited to one of several relatively simple morphology classes (and for which the effects of elastic scattering were neglected). SESSA will enable improvements in the accuracy of quantitative AES and XPS analyses of multi-layered structures.

Future Plans: It is planned to extend SESSA to more complex specimen morphologies, initially the important class of islands on a substrate. Other planned enhancements include the ability to specify the polarization of incident X-rays in XPS (for applications with synchrotron radiation), the addition of newly calculated photoionization cross sections that include non-dipole terms, and the ability to specify the variation of the analyzer transmission function with electron energy.

Impact Energy Dependence of SF₅⁺ Ion Beam Damage of PMMA Films Studied using ToF-SIMS

Matthew S. Wagner (Div. 837)

Program: Chemical Instruments - HTS

Abstract: Recent advances in instrumentation for Secondary Ion Mass Spectrometry (SIMS) have focused on the application of polyatomic primary ion sources for enhancing the molecular secondary ion signals of organic materials. A few studies have also noted that some polymers, in particular poly(methyl methacrylate) (PMMA), display the unusual characteristic of maintaining their molecular ion signals after extended bombardment with polyatomic ion beams. In this study, the damage of ~ 70 nm thick spin cast films of PMMA by SF₅⁺ with impact energies from 2.5 – 8.75 keV was studied using Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS). Sputtering of the polymer using SF₅⁺ was alternated with collection of static positive and negative ion ToF-SIMS spectra to assess the damage created by SF₅⁺ ion bombardment in the ion dose range of 2.5 x 10¹³ – 5 x 10¹⁴ SF₅⁺ ions/cm². All beam energies displayed maintenance of the characteristic molecular ion signals for PMMA despite extended SF₅⁺ bombardment. An increase in the SF₅⁺ bombardment energy increased the sputter rate of the polymer without increasing the accumulation of beam-induced damage. Additionally, neither fluorocarbon cations nor anions were observed in the ToF-SIMS spectra of the damaged PMMA films.

Purpose: The purpose of this project was to determine the effect of primary ion beam parameters, in this case the impact energy, on the damage accrued in PMMA films under SF₅⁺ primary ion bombardment.

Major Accomplishments: We have studied the effect of SF₅⁺ impact energy in the range of 2.5 – 8.75 keV on the damage of PMMA thin films. PMMA thin films (thickness ~ 70 nm) were obtained by spin coating onto silicon wafer substrates. Damage profiles of PMMA under SF₅⁺ bombardment were obtained by alternating the collection of static ToF-SIMS spectra with sputtering using SF₅⁺.

Figure 1 shows the (a) C₄H₅O⁺ (m/z = 69) and (b) Si⁺ (m/z = 28) secondary ion signals as a function of SF₅⁺ primary ion dose and impact energy. The C₄H₅O⁺ secondary ion is characteristic for the PMMA film and the Si⁺ secondary ion is characteristic for the silicon substrate. As the SF₅⁺ primary ion dose increased, the C₄H₅O⁺ secondary ion intensity could be described by three regions. Region (i), characterized by an initial intensity decrease followed by region (ii) with a quasi-stabilization of the secondary ion intensity. After this extended stable regime, region (iii) is characterized by a rapid decay in C₄H₅O⁺ secondary ion intensity as the Si⁺ secondary ion intensity increased, indicating that the polymer film had been sputtered through and the silicon substrate had been exposed. As the SF₅⁺ impact energy increased, the PMMA sputter rate increased (indicated by the reduction in the SF₅⁺ ion dose necessary to reach the silicon substrate). However, the slope of region (ii) in the damage profiles did not increase as a function of SF₅⁺ impact energy, suggesting that changing the impact energy did not change the rate of damage accumulation in the polymer film. These results suggest that the highest impact energy available would be optimal for molecular depth profiling of polymer films.

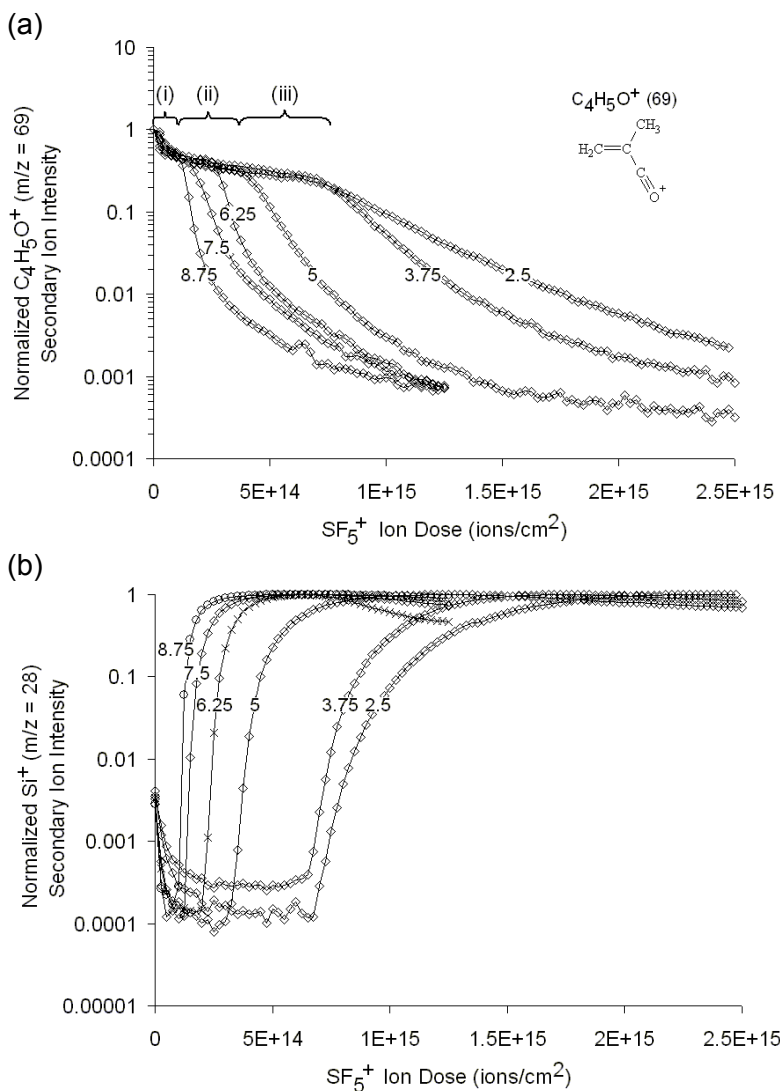


Figure 1. The (a) $C_4H_5O^+$ (m/z = 69) and (b) Si^+ (m/z = 28) secondary ion intensity (normalized to its initial intensity for each damage profile) as a function of SF_5^+ ion dose for impact energies between 2.5 and 8.75 keV. The SF_5^+ impact energy is marked on each of the damage profiles. The $C_4H_5O^+$ secondary ion is characteristic for the PMMA film while the Si^+ secondary ion is characteristic for the silicon substrate. The three regions of the damage profiles are marked in (a) for the 5 keV SF_5^+ damage profile.

Impact: The measurements reported here have demonstrated that the degree of damage accumulated by the PMMA film was not affected by the SF_5^+ impact energy. However, increasing impact energy increased the sputter rate. These results have provided optimized conditions for depth profiling of polymer samples, with the anticipation of aiding in the development of polymeric biomaterials and drug delivery vehicles.

Future Plans: This work has provided an understanding of the SF_5^+ -induced damage on PMMA. Future work will further examine the surface chemical modification of PMMA under SF_5^+ bombardment using X-ray Photoelectron Spectroscopy (XPS) and surface topography development using Atomic Force Microscopy (AFM). In addition, the effect of polymer chemistry on the stability of the polymer film under SF_5^+ bombardment will be examined using a systematically varying set of polymer films. The final goal of this project is the development of polyatomic primary ions for the routine molecular depth profiling of polymeric samples.

Characterization of chemical properties, structural parameters and particle size distribution of three zeolite reference materials

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CSTL Program: Chemical and Allied Products

Abstract: Zeolites encompass a large class of hydrated silicate materials that have structures containing channels and cages of various dimensions. Both synthetic and natural zeolites have widespread industrial applications in petroleum refining, chemical manufacturing, gas separation and dehydration, environmental cleanup, and as ingredients in detergents. Despite their widespread use over the past three to four decades, no materials with characterized physical parameters have been available for intercomparison studies. An NSF sponsored meeting of academic, government and industrial workers specified the need for characterized zeolites and recommended that NIST develop such materials. This work was undertaken to address this need.

Analytical protocols were set up and tested for obtaining chemical and structural data in a controlled humidity environment. Reference and information values related to the chemistry, structure and particle size distributions have been obtained for this industrially important group of materials. These reference materials will provide a basis for intercomparison of zeolite measurements between analytical laboratories.

Purpose: To characterize the chemistry, structural parameters and particle size distribution of three zeolite materials of industrial importance.

Major Accomplishments: Three zeolites were studied – faujasite (FAU), Linde Type A (LTA) and ZSM-5 (MFI). The hygroscopic nature of the materials was a major challenge for the chemical and structural characterization. Materials were handled in a humidity-controlled environment with minimal exposure to ambient environmental conditions. The major element concentrations were determined by x-ray fluorescence analysis (XRF), gravimetry, and instrumental neutron activation analysis (INAA). Their trace element concentrations were determined by INAA. Structural parameters were characterized using synchrotron x-ray diffraction and neutron diffraction. The particle size distributions were characterized by optical and sedimentation techniques.

Impact: Zeolite materials with characterized chemical, structural and particle size parameters are available as reference materials (RM 8850 [FAU], RM 8851 [LTA] and RM 8852 [MFI]). These materials provide a means for intercomparison studies of various techniques used for zeolite analyses.

Future Plans: If warranted, other zeolites may be similarly analyzed.

Trace Nanoanalysis Using Hyperspectral Imaging

John Henry J. Scott and Joseph Conny

Program: Technologies for Future Measurements and Standards

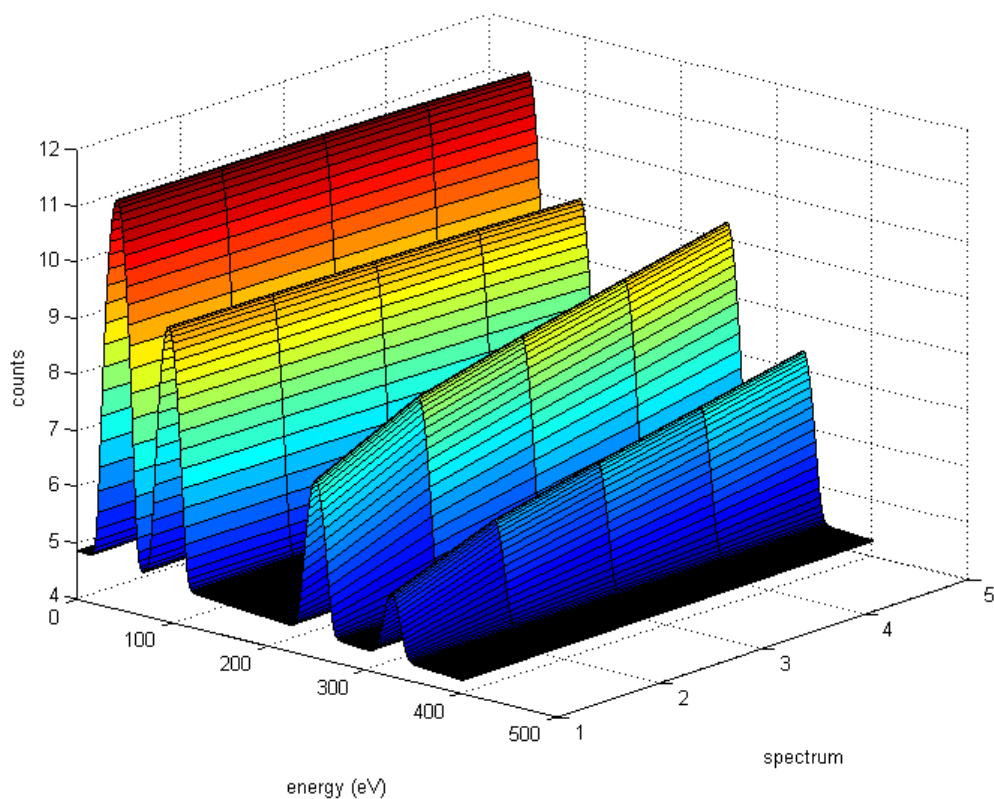
Abstract: The recent introduction of multispectral and hyperspectral imaging techniques to analytical electron microscopy and electron probe microanalysis has led to an explosion in the amount of chemical data available from each sample. Thousands of channels of spectral information can be saved for each of millions of pixels on the specimen, and the challenge is to find techniques that can exploit this wealth of raw data. Following the lead of analytical chemists working with non-microscopic methods, this work attempts to apply multivariate statistical tools and chemometrics to meet this challenge. The goal is to provide a new suite of analysis tools for the microanalysts in government labs, academia, and the industrial sector. The NIST/NIH Desktop Spectrum Analyzer (DTSA) is able to generate synthetic x-ray spectrometry data sets with high fidelity, including both training data and “unknown” compositions for testing new statistical approaches and validating methods such as Principal Components Regression (PCR) and Partial Least Squares (PLS) for multivariate calibration. Software implementing these algorithms (in Matlab) was linked to DTSA output via a series of scripts. This allows ideas borrowed from chemometrics (such as multivariate curve resolution, multivariate image analysis, and inverse calibration methods) to be applied to current problems in microanalysis.

Purpose:

- develop tools and utilities for exploring the application of chemometrics to trace nanoanalysis in the analytical electron microscope (AEM) and electron microprobe
- apply multivariate data analysis strategies developed for bulk analytical methods to chemical analysis at high spatial resolution in the analytical electron microscope

Major Accomplishments:

- implemented a set of scripts for pipelining data from the NIST/NIH Desktop Spectrum Analyzer package (DTSA) to the PLS toolbox in Matlab for multivariate analysis
- developed an environment for testing the viability of existing methods in chemometrics in the context of hyperspectral data acquisition in the AEM and electron microprobe
- imported synthetic Fe-Ni-Cr spectral data from DTSA into Matlab to evaluate Principal Components Regression (PCR) and Partial Least Squares (PLS) as potential methods for multivariate quantitative microanalysis
- imported synthetic datasets for exploring non-linear spectral pre-treatments to optimize multivariate calibration using energy-dispersive x-ray (EDS) data
- used multivariate curve resolution to resolve mixed experimental spectra into “pure components” without a priori chemical knowledge of the system; investigated numerical convergence problems



Surface plot of Nickel-Chromium test hyperspectral dataset generated by DTSA, displayed in Matlab.

Impact:

may permit leveraging of existing expertise in chemometrics to enhance performance of chemical measurement tools such as energy-dispersive x-ray spectrometry

Future Plans:

investigate current topics being explored in analytical chemistry, chemometrics, and multivariate analysis and apply them to problems of ultramicroanalysis of concern to Division 837 and CSTL