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SURFACE AND MICROANALYSIS SCIENCE DIVISION

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, 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, mechanisms, and effects of processes occurring on solid surfaces and interfaces as well as within materials and devices;
4. Study the total chemical measurement process as well as source apportionment in atmospheric chemistry using advanced isotope metrology and chemometrics; and
5. Develop and certify key Standard Reference Materials and Standard Reference Data.

Organizational Structure:

The Division is organized into four 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.

Atmospheric Chemistry Group

- Develops and applies methods for the separation and chemical/isotopic measurement of trace atmospheric gases and particles. Techniques include:
 - Thermal-optical analysis to fractionate carbonaceous matrices
 - GC/MS to speciate carbonaceous matrices
 - Accelerator mass spectrometry for ^{14}C
 - High-precision isotope ratio mass spectrometry (IRMS) for ^{13}C and other light stable isotopes
 - Continuous-flow GC/IRMS for isotopic analysis of nanogram-sized samples

- Investigates chemometric (chemical informatic) methods in applied analytical problems involving multivariate and multicomponent systems.
 - Includes development of theoretical, experimental, and mathematical methods for apportioning natural and anthropogenic sources of carbonaceous gases and particles

Microanalysis Research Group

- Performs research, development, and applications on 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 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

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.
- 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 Raman microprobe
 - Fourier-transform infrared microprobe
 - 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 catalytic, electronic, polymer and photonic applications.
- Develops and applies surface sensitive diagnostics involving lasers, radicals, 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, catalytic, electronic, and nanoscale science.

Division Programs

The Division plays a central role in four of the CSTL programs: Semiconductor Metrology, Nanotechnology, Chemical Characterization of Materials, and Environmental Measurements. Due to the infrastructural character of many of the projects they frequently bring technical benefits to more than one of these four programs.

Semiconductor Metrology

Electronic and advanced materials are increasingly impacted by compositional changes on the submicrometer 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 in FY2001 span energy transfer between oxygen radicals and fused silica surfaces, depth profiling standards for Secondary Ion Mass Spectrometers (SIMS), increased sensitivity for secondary ions in SIMS, and advanced methods for measurement of gate dielectric films:

- “High Precision Measurements of Arsenic and Phosphorous Implantation Dose in Silicon by Secondary Ion Mass Spectrometry” P.H. Chi, D.S. Simons, J.M. McKinley (Agere Systems), F.A. Stevie (Agere Systems), and C.N. Granger (Agere Systems).
- “Influence of Electron Multiplier Post-Acceleration on the Detection of Secondary Ions”, A.J. Fahey.

- “Grazing Incidence X-ray Photoemission Spectroscopy Measurements of Gate Dielectrics: Internal Calibration and Comparison with X-ray and Neutron Scattering”, T. Jach and E. Landree (Guest Worker).
- “Interactions of Ground (3P) and Electronically-excited (1D) State Oxygen Atoms with Fused Silica”, S.A. Buntin and M. Litorja.

Nanotechnology

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 science, catalyst development, and nanoscale device optimization. Improvements in sensitivity coupled with reductions in sample degradation issues 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 to characterize the dielectric response of combinatorial libraries using non-contact methods. The subtle details of chemical structures at interfaces have been probed using non-linear optical methods and the limits of High Resolution Transmission Electron Microscopy for gate dielectric film thickness have been explored. Efforts this year have led to:

- “Mapping of Combinatorial Bio-Surface Test Substrates using TOF-SIMS”, S.V. Roberson, A.J. Fahey, A. Seghal (854) and A. Karim (854).
- “Selective Study of Molecular Order at Interfaces with Vibrationally-resonant Sum Frequency Generation via Thin Film Interference Effects”, P.T. Wilson, L.J. Richter, K.A. Briggman (844), J.C. Stephenson (844) and W.E. Wallace (854).
- “Near-field Microwave Microscopy for Materials Analysis”, S.J. Stranick, S.W. Robey, C.A. Michaels, P.K. Schenck (852) and D.L. Kaiser (852).
- “Accuracy of HRTEM Gate Dielectric Film Thickness Measurements”, J.H.J. Scott.

Chemical Characterization of Materials

Division efforts span numerous challenges in measurement science. These challenges are encountered in the characterization of small particles, probes that can follow reactions of surface layers at atomic dimensions, and the ability to identify major and minor isotopes 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 communities, e.g., DoD, DoE, 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 develops and applies 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, the location and characterization of particles, the development of standards for instrumental analysis, and the formation and structure of buried interfaces. Efforts this year have led to:

- “Autoradiography of Uranium Particles”, C.J. Zeissler, G.P. Lamaze (839) and R.M. Lindstrom (839).
- “Combinatorial Measurements of Nucleated Crystallization in Polypropylene Films, M.L. Walker”, A.P. Smith (854) and A. Karim (854)
- “Imaging and Chemical Characterization of High Explosive Particles using Cluster Secondary Ion Mass Spectrometry”, J.G. Gillen, S. Wight, R. Lareau (FAA).
- “Chemical Imaging of Thin Film Polymer Blends with Near-Field Infrared Microscopy and Spectroscopy”, C.A. Michaels, D.B. Chase (Dupont Co.) and S.J. Stranick.
- “Improved Quantitative Particle Analysis using Low-voltage Electron Beams”, J.A. Small.
- “An In-situ, Vibrationally-Resonant Sum Frequency Spectroscopy Study of the Self-Assembly of Dioctadecyl Disulfide on Au”, C.S.-C. Yang, L.J. Richter, J.C. Stephenson (844), and K.A. Briggman (844).

- “Certification of SRM-2241: Raman Intensity Standard”, E.S. Etz, W.S. Hurst (836), S.J. Choquette (839), and D.H. Blackburn (Contractor).
- “Propagation of Error in the Precision and Accuracy of Quantitative Electron Microbeam Analysis”, J.T. Armstrong
- “Silicon Drift Detector for Rapid X-ray Spectrometric Analysis”, D.E. Newbury, J.A. Small, J. Iwaczyk (Photon Imaging, Inc.), and Shaul Barcan (Photon Imaging, Inc.)

Environmental Measurements

Environmental measurements continue to push the envelope of microanalysis measurement capabilities. Whether dealing with the identification of airborne asbestos, verification of gas mask calibration procedures, or the attribution of fine particulate matter in regional atmospheric studies, microanalysis methods play a critical role. Isotopic, optical, and electron microscopy methods can combine to provide sound scientific basis for future actions. 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:

- "Fine Particulate Matter Source Attribution for Southeast Texas using $^{14}\text{C}/^{13}\text{C}$ Ratios", G.A. Klouda, K. Lemire (Univ. Texas, Austin), D. Allen (Univ. Texas, Austin), and C. Lewis (US EPA).
- "A Decade of Proficiency Testing of Laboratories Involved in the Analysis of Airborne Asbestos", S. Turner, Eric Windsor, Eric Steel, Stefan Leigh (898), and W. Crankshaw (Research Triangle Institute).
- “Verification of Calibration Procedure for Testing Military Gas Masks”, R. Fletcher, M. Winchester (839), Lance King, J. Small, J. Yang (866), and George Mulholland (866).
- “Asbestos Standards for Industrial and Environmental Contaminants”, J.R. Verkouteren.
- “Production of SRM 2784: Filter-Based Fine Particulate Material”, G.A. Klouda, J.J. Filliben (898), H.J. Parish (SRI International), and J.C. Chow (DRI).
- “Accuracy in Determining Atmospheric Elemental Carbon: Understanding the Response Surface of the Thermal-Optical Method”, J.M. Conny and D.B. Klinedinst.

In addition to these four primary program areas, the Division makes targeted contributions in two other CSTL programs: Chemical and Biochemical Data and

International Measurement Standards. The resources of the Division are readily brought to bear on these program areas through natural extensions of current staff interests and activities.

Chemical and Biochemical Data

- “Fractal Dimensions of Particle Perimeters and Surfaces”, D.S. Bright.
- “New Databases for Surface Analysis by Auger-Electron Spectroscopy and X-ray Photoelectron Spectroscopy”, C.J. Powell (837), A.Y. Lee, D.M. Blakeslee, H. Thai, J.R. Rumble, Jr. (SRDP), A. Naumkin, A. Kraut-Vass, A. Joblonski, and W.S.M. Werner (contractors).

International Measurement Standards

- “Development of an International Standard for the Evaluation of Microheterogeneity of Reference Materials for Microanalysis”, R.B. Marinenko, S. Leigh (898), and M. Styles (British Standards Institute)
- “Improvement of Value Assignments for NIST and IAEA Stable Isotope Reference Materials”, R.M. Verkouteren, D.B. Klinedinst, M. Groening (IAEA).

Annual Highlights

Key Technical Achievements

FY2001 marked the culmination of a series of challenging experiments that addressed the reactivity of chemical radicals at surfaces. Through the use of a unique laser-based O atom beam source and state-resolved detection techniques we have characterized at an unprecedented level of detail the interactions of ground (^3P) and electronically-excited (^1D) state O atoms with fused silica surfaces. Atomic oxygen is often the species that dominates the desired surface chemistry in oxygen plasmas, which are used widely in semiconductor processing and for surface modification. While both ^3P and ^1D state O atoms can be present in these plasmas, the reactivities of these species with relevant surfaces are not well characterized. The results provide quantitative information regarding the survival probability of each species and the quenching dynamics of the electronically excited ^1D O atoms. Fused silica is widely used in the generation and containment regions of plasma reactors, and it is anticipated that these results will impact accurate modeling of oxygen plasma systems.

Measurement capabilities within the Division were expanded in FY2001 with installation of a new Field Emission Gun Scanning Auger Microprobe. This instrument has already achieved spatial resolution that is an order of magnitude better than prior generations of this instrumentation. We have demonstrated selective analysis of sub-micrometer (nanoscale) particles on substrates with exclusion of substrate spectral contributions to trace levels. This improved resolution opens new capabilities for chemical

characterization by combining the sensitivity of AES to surface species with the quantitative compositional capabilities of electron probe instrumentation.

Renovation of laboratory space began in FY2001 in anticipation of delivery of a new high resolution/high transmission magnetic sector SIMS instrument in the first quarter of 2002. This new instrument will expand our capabilities to analyze elemental and isotopic species in extremely sample-limited situations such as analysis of individual sub-micrometer particles. Another application with potentially significant impact that we will explore is the detection of transition metal contamination on the surface of silicon wafers. High mass resolution is required for detection of the major iron and nickel isotopes in the presence of silicon dimers in the mass spectrum. Conventional SIMS instruments require a large sacrifice in transmission to achieve the required mass resolution, but the new instrument will have substantially higher transmission, and consequently a significant improvement in detection limits for these elements.

The Division has performed initial performance evaluation tests on silicon drift detector (SDD) technology that appears well positioned to enable significantly higher count rates in electron probe and x-ray fluorescence instruments. Current technology offers a stark choice between energy dispersive spectrometry (EDS) covering x-ray emission from 0.1 to 20 keV, at low total spectrum count rate (~25 kHz), and with 175 eV resolution compared to high count rate (100 kHz or more) wavelength dispersive spectrometry (WDS) with an energy band pass of only 0.010 keV. SDD technology, capable of EDS operation at 500 kHz, could revolutionize microanalysis and process analysis applications. The higher count rates are expected to have significant impacts in high throughput experimentation where current detectors represent the key bottlenecks in microanalysis.

A new technique have been developed that enables *in situ*, non-destructive and selective measurement of buried polymer interfaces by vibrationally resolved sum frequency generation spectroscopy (VR-SFG). Manipulation of Fresnel coefficients through the choice of film thicknesses allows enhancement of the nonlinear optical signal from the desired interface and cancellation of the signal from other obscuring interfacial sources. The VR-SFG spectra reveal that the phenyl group orientation for a buried polystyrene/dielectric interface is in the opposite direction of the phenyl groups at the top free surface. In addition, the molecular ordering at the polymer/dielectric interface changes with changing hydrophobicity of the dielectric surface and correlates to the adhesive strength of the interface. We are pursuing the evaluation of industrially relevant samples to demonstrate the unique measurement capability of VR-SFG with regard to detailed structure of buried polymer interfaces.

This year, Division activities in the area of High Throughput Methods for Combinatorial Chemistry have seen significant expansion. The efforts in high throughput screening are being directed at the development of measurement methods capable of providing validated measurements in the combinatorial setting. In addition, Division staff are developing instrumentation capable of extracting multi-spectral information from the arrays of small samples that comprise combinatorial methods. Specific applications of

microanalysis methods to combinatorial systems can be seen in the SIMS work on Bio-Surface Test Substrates, where libraries of gradient polymer films were evaluated. Additional work was undertaken to characterize compositionally graded Barium-Strontium-Titanate films. Electron beam micro characterization was undertaken to establish the variation of film composition as a function of position in the library. The libraries were also characterized using non-contact dielectric spectroscopy to correlate the dielectric properties with variations in film composition. These efforts are being undertaken with partial support from ATP and in collaboration with staff in MSEL where the films are generated and ITL where data mining tools are being developed.

Additional collaborative efforts in FY2001 have included: A Competence Proposal in the area of Optoelectronics (with MSEL, EEEL, and Division 836), initiation of a new program in Molecular Electronics (with Divisions 836, 838, and EEEL) that includes experimental and theoretical efforts, and ongoing activities in the environmental arena that span Division 836 and 839.

Technical Achievement Award for FY2001 – was presented to Chris A. Michaels, Stephan J. Stranick, Lee J. Richter, and Richard R. Cavanagh, for their paper “*Scanning near-field infrared microscopy and spectroscopy with a broadband laser source.*” *Journal of Applied Physics* **88**, 4832-4839 (2000). This paper provides a concise summary of the near-field microscopy and spectroscopy capability that was developed in the Division. By incorporating infrared spectroscopy with near-field microscopy, the ability to differentiate chemical species based on a widely accepted contrast mechanism has been achieved. The paper discusses the instrument design, including a state-of-the-art light source, a unique optical collection geometry, a novel infrared detector array, and fabrication of the scanned tips. Methods for evaluation of the spatial resolution of the instrument are presented, as are methods for determining the sensitivity for typical infrared absorbers. In addition to discussing the operational basis of the instrument, the paper presents examples of the utility of this measurement approach on samples spanning metal islands on silicon, titanium dioxide particles embedded in a polymer film, and polystyrene films on silicon. These examples provide a clear indication of the range of samples for which this measurement capability can provide unique information.

Accessibility of Division Outputs

In FY2001, the Division developed a new Web site to improve access to current activities and to identify technical expertise and CSTL program efforts within the Division. The Division web page now makes available information on current Division staff, Division/Group structure, Measurement Expertise, Examples of Program Accomplishments, and Standards and Software (directly downloadable). In addition, the revised web page provides recent updates on meetings and Division news items. Visitors to the site will find direct access to most information of interest, and the opportunity to “Ask a Measurement Question” should the information of interest not be supported on the Web.

To address a fundamental need in stable isotope metrology, the Atmospheric Chemistry Group has established an interactive Common Gateway Interface (CGI) accessible through an internet site (<http://www.nist.gov/widps-co2>) designed to promote the proper usage of isotope reference materials and improve the quality of reported data. This CGI has been designed especially to benefit the atmospheric and health communities that collect and evaluate isotopic data from extensive monitoring networks. Such information is used to formulate effective pollution control strategies for a wide variety of carbonaceous species, including airborne particulate matter, hazardous air pollutants, and “greenhouse” gases. Users may wish to validate proprietary algorithms embedded in their laboratory instrumentation, or specify the values of fundamental variables usually fixed in reduction algorithms to see the effect upon the calculations. Several international laboratories have independently verified the accuracy of the algorithm for natural abundance measurements, as well as slightly enriched compositions up to about 150 % relative to normal abundances of ^{13}C and ^{18}O . In using this Website, improvements of about a factor of four have been realized in reproducibility across laboratories in reported ^{13}C and ^{18}O values. Future plans for the Website include improving the browser interface, incorporating uncertainty estimation, and expansion to include other chemical-isotopic species.

In addition, Web Server Statistics for the NIST Standard Reference Data web site indicate that approximately 30,000 requests are received each month for the XPS database. Requests for this database are an order of magnitude greater than any of the other databases that reside on this server, indicating the broad utilization of this data.

In an ongoing effort to reduce the time required to meet the ever-expanding call for reference materials, the Division has begun to explore an alternate to the SRM and RM approach currently utilized by the NIST Standard Reference Materials Program. The trial approach is designed to quickly make new materials available to interested parties, but without the time consuming, multiple laboratory analyses associated with RMs or the certification that accompanies an SRM. These materials would be donated by interested parties, NIST would distribute the material to private sector analysts, the analysts would submit their data to a NIST IM Web site, and NIST staff would evaluate and post the collective results. To reflect the interactive nature of this process, these materials would be identified as Interactive Materials (IMs).

Assessment of Measurement Needs

The Division organized and participated in technical workshops and conferences with the objective of assessing measurement and standards needs across our broad customer base. These efforts provide key input in our effort to prioritize standards needs and to focus our efforts.

The *Vision 2020 Roadmap for Combinatorial Methods* was finalized and released in FY2001. This report is currently available at <http://www.chemicalvision2020.org/roadmaps.html>, providing an overview of the needs in areas from informatics to library characterization. Responding to a recurring need that was expressed during the development of this roadmap, NIST is evaluating an open

forum that would address technical challenges in high throughput experimentation. A meeting to discuss the utility of a NIST Combinatorial Methods Center (NCCM) was held on July 10, 2001. The meeting was jointly hosted by MSEL, BFRL, and CSTL, with participation from a dozen companies with interests in high throughput experimentation. This meeting resulted in a detailed discussion of mechanisms for collaborative research efforts, ranging from workshops to joint projects.

A workshop was convened in September 2001 entitled “*Atmospheric Measures and Standards: Improving the Scientific Basis for Informed Decisions on Atmospheric Issues.*” This forum, jointly sponsored by CSTL/NIST and NOAA, provided a valuable opportunity to meet with several industry sectors and to gather information on the measurements and science that underpin sound environmental actions. A clear consensus emerged regarding the importance of particle standards in the PM_{2.5} arena. Current efforts with Division 837 and 839 that are funded in part by EPA were well received as sorely needed standards in support of PM_{2.5} issues. Additional activities to refine and focus the environmental effort within CSTL are underway.

The Surface and Microanalysis Science Division co-sponsored the 14th Annual Workshop on Secondary Ion Mass Spectrometry that was held in Phoenix, AZ in May, 2001. In order to assess future microanalysis standards needs for U.S. industry, a special standards session was organized by the division. The session was attended by 120 participants: 75 from industry, 20 from government laboratories and 25 from university labs. After an opening presentation on NIST standards, representatives from several companies including: Motorola, Exxon, DuPont and Charles Evans and Associates gave presentations on standards needs for their respective industries. This was followed by an open discussion session. Feedback on the session provided the Division a very useful perspective on industry needs and has led to plans to develop a suite of SiGe standards which were identified as a critical need for the semiconductor industry.

Interactions:

The Division is involved in advisory and technical efforts with other government organizations including EPA, IAEA, NSF, Treasury, DoD and DoE. 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: Agere, Ceramem, Charles Evans & Assoc., Dow Chemical, Dow Corning, DRI, DuPont, Kodak, McCrone Assoc., Merck Sharp and Dome Pharmaceuticals, Noran, Peabody Scientific, Photon Imaging, Schafer Vallecitos Laboratories, SRI, 3M, Visteon, and XOS, Inc.

Autoradiography of Uranium Particles

CSTL Program: Chemical Characterization of Materials

Authors: C.J. Zeissler; G.P. Lamaze, and R.M. Lindstrom (839)

Abstract: NIST has led the establishment of a secondary ion mass spectrometry (SIMS) program at the International Atomic Energy Agency (IAEA) for uranium isotope measurements of particles collected by cloth swipes. We are investigating the addition of an autoradiography method to improve the overall detection sensitivity of the SIMS measurements. These improvements will assist the IAEA in their programs for nuclear safeguarding and international treaty verification.

Swipes typically contain tens of milligrams of particulate matter, with perhaps only a few picograms of uranium particles. A SIMS analytical session measures less than a microgram of particulate matter so the entire swipe cannot be analyzed. Some form of sub-sampling must be performed first. Autoradiography of the swipe prior to sub-sampling may be used to increase the number of uranium particles that will be analyzed. However, autoradiography takes time, and sensitivity and discrimination are degraded by geometrical and attenuation effects. Uranium discrimination and detection sensitivity have been studied to evaluate the level of advantage offered by adding autoradiography prior to SIMS.

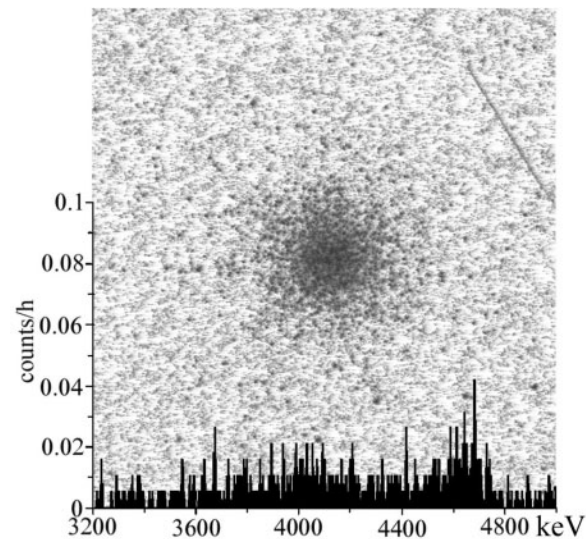


Figure 1. Eight-day alpha spectrometry plot and eleven-day autoradiograph showing a cluster of alpha-particle counts from a 0.005 Bq uranium particle. The field-of-view is approximately 1 cm.

Purpose: To provide measurement developments and characterization used to improve nuclear safeguarding and verification efforts conducted by the International Atomic Energy Agency (IAEA), a United Nations organization. NIST is continuing a program to assist the IAEA in the establishing and improving SIMS measurements, often being called upon to help with sample preparation, measurement quality, and sensitivity concerns.

Major Accomplishments in FY2001: Theoretically, the location of a nanogram particle of natural uranium can be mapped by a two-week autoradiography count, whereas a 20% enriched uranium particle (an enrichment level of particular interest to the International Atomic Energy Agency), may be mapped at the few-picogram level in the same time period. Single particles of natural and highly enriched uranium were individually mounted on substrates and used to compare results to the theoretical optimal detection limits. The sensitivity of the autoradiography method was demonstrated by comparison to

gamma spectrometry and alpha spectrometry. The particle associated with Figure 1 was undetectable by low-background gamma spectrometry, and the ease of visual recognition of the presence of uranium in the alpha spectrum was poor (Figure 1). However, the alpha particle signature of the uranium in the autoradiograph is easily recognizable and would also be easily discriminated in much shorter exposures.

Impact: NIST contributes to the potential advancement of world-wide security because uranium detection sensitivity improvements could make it more difficult for IAEA member states to utilize nuclear materials for non-peaceful purposes.

Future Plans: Future efforts will purposefully degrade the measurement conditions to match a variety of real-world scenarios. The lower limit of detection for natural uranium for a best-case scenario will be tested. We also plan to more fully cover a range of enrichment levels by using a series of reference materials from depleted (DU) to highly enriched (HEU). Parameters to test include the presence of sample containment materials, the physical depth of the particles in the cloth wipe, interference by non-uranium particles, and the discrimination of background from attenuated sample signals for various exposure durations.

New Databases for Surface Analysis by Auger-Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

CSTL Program: Physical Property Data

Authors: *C.J. Powell; A.Y. Lee, D.M. Blakeslee, H. Thai, and J.R. Rumble, Jr. (SRDP); A. Naumkin, A. Kraut-Vass, A. Jablonski, and W.S.M. Werner (Contractors)*

Abstract: During the past year, a new version of the popular NIST X-Ray Photoelectron Spectroscopy Database (SRD 20) was released, the new NIST Electron Effective-Attenuation-Length Database (SRD 82) was released, and work advanced on a new NIST database for Quantification of Electron Spectroscopic Techniques (QUEST).

- SRD 20 provides identification of unknown spectral lines in user measurements, retrieval of data for selected elements, retrieval of data for selected compounds, and retrieval of data by scientific citation. From January to July 2001, there were approximately 30,000 requests per month for information from this database.
- SRD 82 provides values of electron effective attenuation lengths and related data for AES and XPS. Values of effective attenuation lengths (EALs) are needed mainly for measurements of thicknesses of overlayer films and to a much lesser extent for measurements of the depths of thin marker layers. SRD 82 was released in September, 2001.
- Work is well advanced on the new QUEST database to be used for AES and XPS analyses of materials with complex morphologies. This database will access data from SRD 64 and SRD 71 and, with additional data, will enable comparisons to be made of measured and simulated spectra for particular specimen morphologies and specified analytical conditions.

Objective: To provide needed reference data for surface analyses by Auger-electron spectroscopy (AES) and X-Ray photoelectron spectroscopy (XPS).

Problem: Surface properties are crucial for the fabrication and performance of a wide range of materials, semiconductor devices, optoelectronic materials, high-density magnetic-storage media, sensors, catalysts, thin films, and coatings. Surface analysis is used not only to correlate the composition of an exposed surface with specific material properties but also for the investigation of interface properties. AES and XPS are the two most commonly used techniques for surface analysis, and reference data are needed to improve the reliability and efficiency of surface analyses made by these techniques.

Approach: NIST established a Surface Analysis Data Center in 1997 to give greater visibility to its existing and planned databases for applications in surface analysis. The development of databases is carried out with the NIST Standard Reference Data Program and with the assistance of contractors.

Results and Future Plans: During the past year, a new version of the popular NIST X-Ray Photoelectron Spectroscopy Database (SRD 20) was released, the new NIST Electron Effective-Attenuation-Length Database (SRD 82) was released, and work advanced on a new NIST database for Quantification of Electron Spectroscopic Techniques (QUEST). These developments will be described in turn.

SRD 20 provides identification of unknown spectral lines in user measurements (for photoelectron lines, Auger-electron lines, Auger parameters, and doublet separations), retrieval of data for selected elements (binding energies, Auger-electron kinetic energies, chemical shifts, surface and interface core-level shifts, and elemental reference data), retrieval of data for selected compounds (for selected groups of elements, chemical names, chemical classes, and compounds containing a selected element), display of Wagner plots (Auger-electron kinetic energy versus binding energy for compounds containing a selected element), and retrieval of data by scientific citation. Version 3.0 of SRD 20, an Internet version, was released in 2000. This version included a significant amount of additional data and, for the new data, additional information on the specimen material, the measurement procedure, and the data-analysis procedure for each reported measurement. The screens were redesigned to facilitate user access, user searches, and user convenience. Version 3.1, released in 2001, provides an expanded capability for displaying Wagner plots; these plots can now be prepared for 42 elements. Versions 3.0 and 3.1 of SRD 20 have been widely utilized. From January to July 2001, there were approximately 30,000 requests per month for information from this database. Work is ongoing to provide additional evaluated data for this database.

SRD 82 provides values of electron effective attenuation lengths and related data for AES and XPS. Values of effective attenuation lengths (EALs) are needed mainly for measurements of thicknesses of overlayer films and to a much lesser extent for measurements of the depths of thin marker layers. The EAL differs from the corresponding electron inelastic mean free path (IMFP) by up to about 35% for common measurement conditions due to elastic scattering of the signal electrons in the specimen material. EALs are computed from transport mean free paths (from the NIST Electron Elastic-Scattering Cross-Section Database, SRD 64) and IMFPs (from the NIST Electron Inelastic-Mean-Free-Path Database, SRD 71) using an algorithm based on electron transport theory for measurement conditions specified by the user. EALs can be found for elements and compounds for electron energies between 50 eV and 2,000 eV, the range of practical interest for AES and XPS. SRD 82 was released in September, 2001.

Work is well advanced on the new QUEST database to be used for AES and XPS analyses of materials with complex morphologies. This database will access data from SRD 64 and SRD 71 and, with additional data, will enable comparisons to be made of measured and simulated spectra for particular specimen morphologies and specified analytical conditions. Satisfactory comparisons of measured and simulated spectra will enable a user to obtain morphology and composition information for a particular specimen. Initially, QUEST will be limited to specimens consisting of layered materials but it is planned later to develop the capability to simulate spectra for specimens with three-dimensional inhomogeneities.

Influence of Electron Multiplier Post-Acceleration on the Detection of Secondary Ions

CSTL Program: Microelectronics

Author: *A.J. Fahey*

Abstract: The International Technology Roadmap for Semiconductors (ITRS) defines a critical need for improved secondary ion mass spectrometry (SIMS) capabilities for ultrashallow dopant profile measurements and improved accuracy for dopant dose measurements. In order to measure shallow dopant profiles, low energy Secondary Ion Mass Spectrometry (SIMS) is employed, which involves reduction of both the primary and secondary ion energy. Reduction of the secondary ion energies in SIMS can reduce the detection efficiency in an element-dependent way so that standard relative sensitivity factors are no longer valid. In addition, the use of lower energy secondary ions results in reduced detection efficiency with electron multiplier detectors. We have installed a secondary ion post-acceleration system on our magnetic sector SIMS electron multiplier detector in order to study these effects. It was found, as suspected, that relative electron multiplier detection sensitivities, such as those for B and Si, change with secondary ion energy. The post-acceleration system allows us to minimize these sensitivity variations which should lead to improved dopant quantification for the semiconductor industry.

Purpose: This work is part of a continuing effort to improve quantification of SIMS measurements of semiconductors with an emphasis on development of techniques to address the rapidly decreasing dimensions of semiconductor devices. Quantification of relative sensitivity factors plays a key role in determining dopant levels and depth profiles.

Major Accomplishments: The post-acceleration and detector system of the NIST IMS-4f was modified so that pulse height distributions could be obtained automatically via a Labview interface. Ideally, the pulse height distributions obtained from an electron multiplier in a mass spectrometer should be peaked, and not exponential. This allow for setting of the threshold at the low-voltage valley of the distribution and provides optimal exclusion of noise while maximizing the number of ions detected. Pulse height distributions were obtained for numerous elements and molecular species each at a range of voltages. The characteristic of each distribution were computed and compared (*e.g.* the mean, variance and integrated intensity vs threshold). It was found that for some elemental species, with generally poor detection efficiencies, that up to a 30% gain in detection efficiency could be achieved by raising the energy of the ions incident on the detector from 4.5 keV to 10 keV. Larger gains in detection efficiency were obtained for molecular species. However, most importantly, it was measured that the relative sensitivity of B to Si can change by more that 10% at low secondary ion energies without the aid of ion post-acceleration for detection, whereas there is no change at 8 keV of post acceleration over a wide range of detector threshold voltage settings.

Impact: SIMS is widely used in the semiconductor industry to characterize dopant profiles. We have shown that care must be taken during quantification of the ion signals

especially if post-acceleration is not employed to enhance the ion detection efficiency when using low secondary ion extraction voltages. In addition, we have demonstrated that significant gains in detection efficiency can be achieved for both elemental and molecular species if detector post-acceleration is used.

Future Plans: We plan to develop experimental procedures for optimizing electron multiplier setup for the analysis As, P and B dopants in silicon. This procedure will be developed as into an ASTM standard practice for SIMS analysis.

Propagation of Errors in the Precision and Accuracy of Quantitative Electron Microbeam Analysis

CSTL Program: Chemical Characterization Of Materials

Author: *J.T. Armstrong*

Abstract: A practical series of quality control procedures were developed and an evaluation of microprobe correction algorithms was made to provide a robust estimate of attainable accuracies in conventional quantitative microbeam analysis. These procedures enable analysts, for the first time, to have a clear-cut and practical method to make a realistic estimate of the accuracy of an SEM or electron microprobe analysis. Factors such as beam stability, faraday cup accuracy, counting linearity, and spectrometer reproducibility were determined. The magnitude of systematic errors to be expected from random instrumental artifacts (such as stage drift, spectrometer detuning, detector bias variations, and accelerating potential fluctuations) were determined. The effects of factors such as charging, surface contamination, specimen roughness and tilt were determined by a combination of experimental measurements with thin-film and Monte Carlo calculations. The magnitude of random and systematic errors due to inaccuracies in the background subtraction and spectral deconvolution procedures were calculated. Initial results of these experiments were reported at the Microscopy and Microanalysis 2001 meeting. An initial test version of some of the associated software is available on <http://www.cstl.nist.gov/div837/Division/outputs/software.htm>.

Purpose: A common question, but one typically difficult to answer, is “How accurate is a microprobe or SEM analysis?” Commercial software for most EDS and WDS systems print out error limits that are typically calculated standard deviations based on Gaussian counting statistics for the accumulated peak and background counts. This is not a true measure of even the measurement precision, since random instrumental instabilities typically degrade “true” measurement precision (as determined by replicate measurements on standards) to 1.5 – 3+ times that predicted from Gaussian statistics. In addition to these random instrumental variations are a plethora of possible systematic and semi-random errors due to sample preparation and instrumental artifacts.^{1,2} Finally, in order to determine analytical accuracy, the compositional differences between standards and sample and the relative accuracy of the physical models and parameters used in the correction procedures need to be evaluated. The magnitude of imprecision and inaccuracy due to these latter factors has been hard to estimate. This has limited the ability of analysts to report realistic levels of precision and accuracy for their analyses – particularly when working with materials of unfamiliar composition. Thus, although microbeam analysis is potentially one of the most accurate analytical techniques, it has been typically quite difficult for analysts in this field to comply with the tight requirements of quality assurance.

Major Accomplishments: We have developed a practical series of quality control procedures and an evaluation of microprobe correction algorithms to provide a robust estimate of attainable accuracies in conventional quantitative microbeam analysis. Factors such as beam stability, faraday cup accuracy, counting linearity, and spectrometer

reproducibility were determined by replicate measurements on homogeneous standards under appropriately varied analytical conditions. The magnitude of systematic errors to be expected from random instrumental artifacts (such as stage drift, spectrometer detuning, detector bias variations, and accelerating potential fluctuations) were determined by making precise sets of measurements under controlled, varying degrees of detuning for critical instruments. The effects of factors such as charging, surface contamination, specimen roughness and tilt were determined by a combination of experimental measurements with thin-film and Monte Carlo calculations³. The magnitude of random and systematic errors due to inaccuracies in the background subtraction and spectral deconvolution procedures were calculated from a combination of experimental measurements and simulations using the NIST DTSA program.⁴ The uncertainties in accuracy due to the correction procedures were calculated by processing the same data through a variety of combinations of currently used parameters and correction algorithms, and calculating the standard deviation of the spread of the calculated data using a new NIST program (“TRYZAF”) based on the original CITZAF correction package.⁵ Initial results of these experiments were reported at the Microscopy and Microanalysis 2001 meeting.⁶ An test version of “TRYZAF” is available at <http://www.cstl.nist.gov/div837/Division/outputs/software.htm>.

Impact: The use of a combination of quality control experiments and data simulation, such as developed in this program, can provide a much more realistic estimate of the full precision and accuracy of microprobe analyses and be helpful in the documentation for ISO 9000 compliance. One can use these methods to predict the level of precision and accuracy that can be achieved in a microbeam analysis for a given class of materials using given standards. In particular, one can use the TRYZAF program to determine the degree of uncertainty in the *accuracy* of an analysis that can be achieved using one set of standards vs. another, based on the differences in results calculated with different sets of correction procedures and physical parameter data bases (such as the different tables of x-ray mass absorption coefficients commonly in use). This capability has not been readily available to the microprobe analyst before, yet is a very important parameter to report (and try to optimize). This has significant impact in establishing the reliability of SEM and microprobe analyses across the wide spectrum of commercial and industrial applications for these techniques.

Future Plans: We plan to further refine and test the instrumental quality assurance measurement procedures we have developed using the various electron microbeam analysis instrumentation in our Division, extending our detailed studies to include *energy* dispersive x-ray analysis (our studies to date have concentrated on *wavelength* dispersive analysis). We intend to publish these as a series of step-by-step quality assurance procedures (with expected typical levels of precision and accuracy) that can be routinely performed in industrial and commercial laboratories with a minimal set of standard materials. We plan to make available on our website a revised NIST version of the CITZAF correction procedure that calculates estimated uncertainties in precision and accuracy due to 1) counting statistics, 2) uncertainties in the subtraction and deconvolution algorithms, 3) instrumental fluctuations and artifacts, 4) sample- and

sample preparation-dependent artifacts, and 5) uncertainties in the physical parameters and correction algorithms used in the calculation of the composition.

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Imaging and Chemical Characterization of High Explosive Particles Using Cluster Secondary Ion Mass Spectrometry

CSTL Program: Chemical Characterization of Materials

Authors: G. Gillen, and S. Wight; R. Lareau (Federal Aviation Administration)

Abstract: Trace explosives detection portal (TEDP) systems are currently under evaluation at the FAA for the noninvasive and rapid identification of airline passengers that may be carrying explosives. The portal systems rely on the collection and preconcentration of explosive particles and vapors that are dislodged from the passenger as they pass through the portal device. Explosive particles are collected on a metallic surface and undergo subsequent thermal desorption for detection by ion mobility spectrometry or time-of-flight mass spectrometry. The aim of our work is to explore the capability of secondary ion mass spectrometry (SIMS) for the spatially resolved analysis of individual explosive particles on TEDP collection media and other model surfaces. The NIST-developed cluster SIMS technique was used for this analysis due to large enhancements in secondary ion signal and a reduction in beam-induced degradation of the samples compared to conventional SIMS analysis. The use of energetic cluster bombardment of explosive particles allows for the rapid screening of explosive particle distributions on collector surfaces using an automated SIMS particle searching technique. This approach allows individual explosive particles to be identified, localized, counted and sized. This capability should be valuable for characterizing the operational characteristics and performance capabilities of TEDP detection systems.

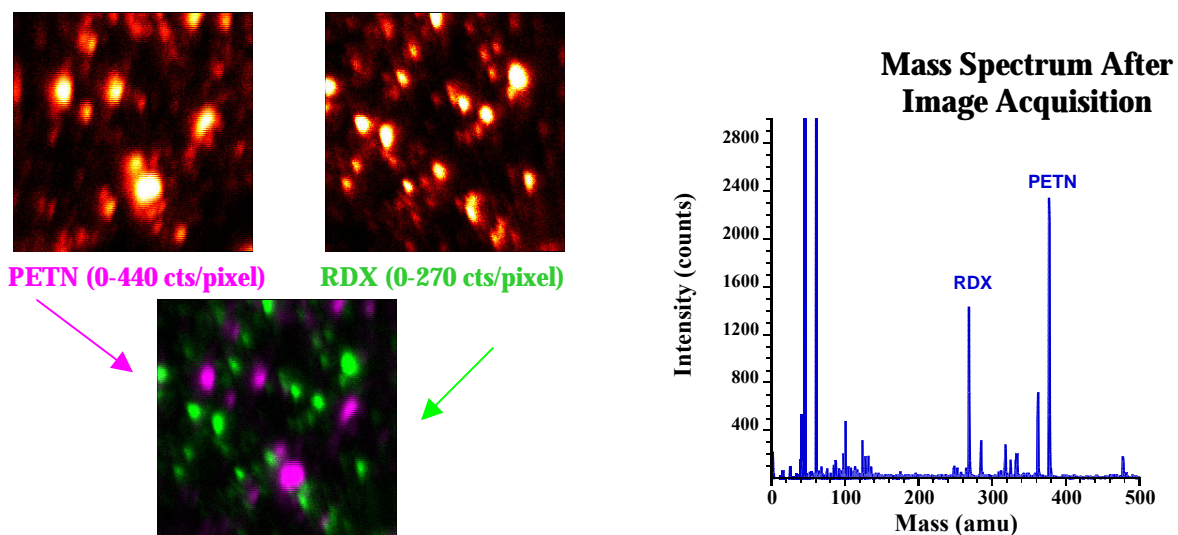


Figure 1. Cluster SIMS secondary ion image of the intact molecular ions from a mixture of RDX and PETN explosive particles dispersed on a silicon collector surface. Field-of-view is 400 micrometers. Image acquisition time was 30 seconds for each compound.

Purpose: The goal of our work is to explore novel microanalytical approaches for the identification of micrometer-sized high explosives particles. This work may aid in the determination of the operational characteristics and performance of trace explosive detection

portals being used by the FAA airport security division. The successful development of a SIMS-based single-particle high explosive characterization technique may also be beneficial for a wide variety of forensic, law enforcement and environmental applications.

Major Accomplishments in FY2001: For this work, samples of RDX, TNT, PETN, C4 and SEMTEX were obtained from the airport security division of the FAA. Samples were deposited as particulates onto silicon wafer slices or stainless steel mesh TEDP collector surfaces. Samples were analyzed using a C_8^- cluster primary ion beam with detection of negative secondary ions. Characteristic mass spectra were obtained from individual particles of the pure materials without difficulty. Representative spectra were also obtained from the more complex C4 and SEMTEX samples which are military plastic explosives containing mixtures of explosives, fuel oil and plasticizers. The larger carbon cluster primary ion beams demonstrated significant improvements in secondary ion yield compared to conventional SIMS analysis. For example, secondary ion yields for the molecular ions of the various explosives were 200-500 times greater using a C_8^- cluster ion beam as compared to the use of a C_1^- ion beam under identical conditions. In addition, beam-induced degradation of explosive particles under cluster bombardment is substantially reduced. The unique resistance of explosives to beam-induced degradation allows for the characterization of explosive particle distributions using automated SIMS particle searching. In this analysis, SIMS images of the molecular ions of each explosive are obtained under high primary current bombardment conditions. The images of each molecular ion are stored in the computer (20s integration times per molecule are used) and the instrument sample stage is stepped to an adjacent position under computer control. This process is continued until a map of the distribution of the explosive particles on the surface is generated. Post processing of the image data allows the explosive particles to be individually identified, localized, counted and sized.

Impact: Characterization of the performance characteristics of explosive detection portal systems is of significant importance for the FAA and national security issues. The rapid analysis of explosive particles may also have forensic and environmental applications that we have not yet explored.

Future Plans: The preliminary feasibility of using cluster SIMS for detection of individual explosive particles has been demonstrated. In the next fiscal year a wide range of other explosives will be analyzed to determine the general applicability of the technique. Further efforts will be made to analyze explosives directly from the TEDP collection grids. We will also study the temperature dependence of desorption from the collector surfaces.

Fractal dimensions of particle perimeters and surfaces

CSTL Program: Physical Property Data

Author: *D.S. Bright*

Abstract: The shape and surface texture of a particle can help to classify or identify it and may also be indicative of its chemical composition or the process through which it was created. Shape and texture are used routinely by humans viewing objects, while only a handful of parameters, such as roundness or root mean square roughness, are routinely available for particle characterization using image analysis. Since the fractal dimension of a boundary or surface seem visually related to its roughness or tortuosity respectively, we wish to investigate the applicability of these dimensions for the description of the shape and texture of individual grains of particulate matter. These physical objects by their very nature do not have true fractal shapes, but we hope that they do exhibit fractal-like behavior in a limited size range (the “local fractal dimension” or LFD). After investigation of some image processing methods in the literature, we have chosen and refined two, to characterize the LFD of the projected boundary of a particle and the LFD of an averaged brightness profile representing the surface. These measurements require the particle to be segmented from background, a tedious task to perform manually and a problematic one to do automatically. We have developed operator-aided segmenting methods that are designed for the image data sets under study.

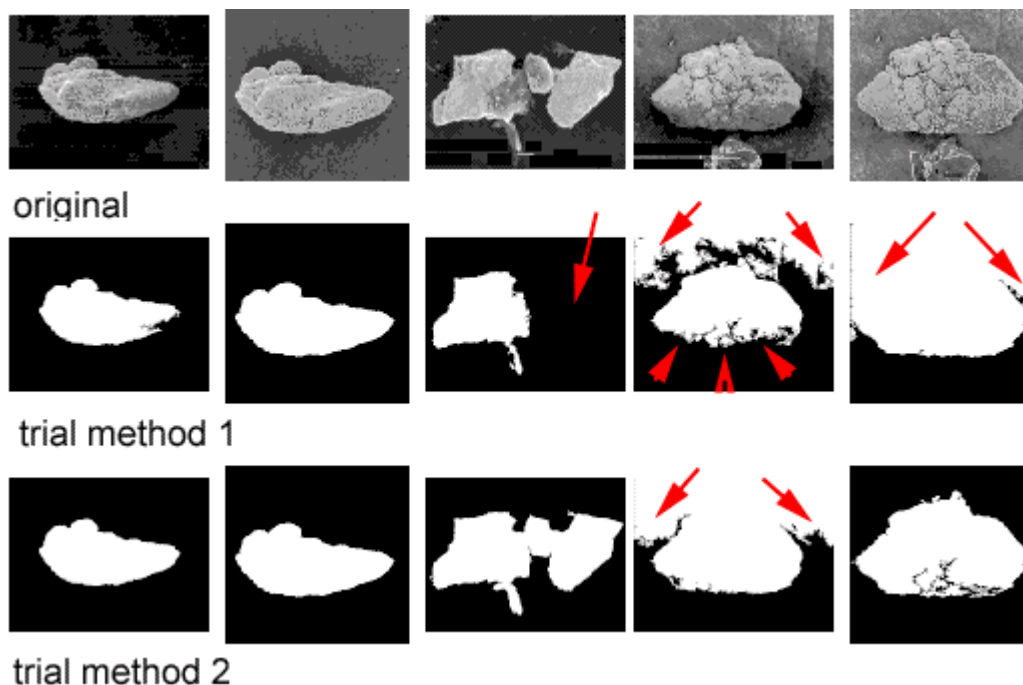


Figure 1. Sample of images from one data set, and results of two trial segmentation methods, which should label one particle per image as white. Arrows indicate more obvious errors.

Purpose: If the LFD's prove to be useful for classifying particles by shape and texture, they may be useful in classifying specific collections of particles by chemical composition or formation process. This is useful because the LFD's are obtained from scanning electron micrographs, which are much easier to obtain than particle history or even chemical composition. The primary customers for this project are particle synthesis industries (catalysis, pigments, cosmetics, etc.), those that perform environmental analysis and monitoring, and groups that characterize process failure due to particle contamination (e.g., pharmaceutical, optoelectronics, and semiconductor industry.)

Major Accomplishments: Robust segmentation methods were developed. Their reliability and applicability were tested for three large image data sets.

Impact: Segmentation is a major problem for image analysis. The segmentation approaches developed here are already being used in several different applications (see customers above). Frequently people analyzing images are forced to segment by hand leading to imprecise data and large expense, making particle population analysis unrealistic. These new segmentation approaches allow most particles to be segmented automatically, a key capability for high throughput experimentation applications. The approach also includes a mechanism to flag most objects that are not segmented properly, so that a manual approach can be used on the small number of particles for which the algorithms fail.

Future Plans: Now that we have image collections and segmentation methods, we will segment the particle images, and determine the LFD's – the latter involves determining the appropriate size range to use. Then, we will visually inspect sorted image sets to see if the LFD's give visually reasonable results, and if so, we will search for any correlations of LFD with chemical data (previously obtained for the major image data set) and process information.

Interactions of Ground (^3P) and Electronically-Excited (^1D) State Oxygen Atoms with Fused Silica

CSTL Programs: Microelectronics, and Chemical Characterization of Materials

Authors: *S.A. Buntin, and M. Litorja*

Abstract: Oxygen plasmas are important in a wide range of industrial applications, including semiconductor processing and surface modification. Atomic oxygen is often the species that dominates the desired surface chemistry in these plasmas. While both ground (^3P) and electronically-excited (^1D) state O atoms can be present, the reactivities of these species with relevant surfaces are not well characterized. In this work, state-specific detection techniques are used to characterize the dynamics of ^3P and ^1D state atomic oxygen interacting with fused silica. The results indicate that the survival probability for ^3P ground state is close to unity, while the ^1D survival probability is less than $\approx 1\%$. The $\text{O}(^3\text{P})$ velocity distribution indicates that only about 5% of the incident ^1D quenches via the formation of super-elastic ^3P species, and about 60% of the scattered ^3P species have velocities characteristic of the surface temperature. Fused silica is widely used in the generation and containment regions of plasma reactors, and it is anticipated that these results will significantly impact accurate modeling of oxygen plasma systems.

Purpose: Because of their unique characteristics, oxygen plasmas are important in a number of industrial applications, ranging from semiconductor processing to surface modification and biocompatibility. Reactive atomic oxygen is often the species that dominates the desired surface chemistry in these plasmas. While both ground and electronically-excited state O atoms can be present, the absolute and relative reactivities of these species with relevant surfaces are not well characterized. Indeed, it has been proposed based on gas phase kinetic data, that metastable $\text{O}(^1\text{D})$ may exhibit surface reactivities that are two orders of magnitude higher than that of ground state O atoms. In this work, the reactivity and dynamics of ground and electronically-excited O atoms with fused silica are probed. These results provide key information on the energy accommodation and survival coefficients of these species on a nominally passive (i.e., nonreactive) surface. Since fused silica is widely used in the generation and containment regions of plasma reactors, the results provide crucial data needed for accurate modeling and optimization of these systems.

Major Accomplishments: The dynamics of ground (^3P) and electronically-excited (^1D) state atomic oxygen interacting with a polished fused silica are characterized using state-resolved detection techniques. A 157 nm F_2 laser is used to produce hyperthermal O atoms ($E_{\text{trans}}=0.39$ eV) from the photolysis of O_2 . Resonance-enhanced multiphoton ionization is used to selectively probe the incident and scattered species for both electronic states, with information on the velocity distribution provided by time-of-flight measurements. For O atom scattering from room temperature silica, the results indicate that the survival probability for ^3P ground state is close to unity. No scattered electronically-excited $\text{O}(^1\text{D})$ atoms were observed, and based on the estimated detection limit, the ^1D survival probability is less than $\approx 1\%$. As shown in Figure 1, the scattered $\text{O}(^3\text{P})$ atom velocity distribution indicates that only about 5% of the incident ^1D quenches

via the formation of super-elastic (i.e., kinetic energy of the scattered product greater than that of the incident species; that is scattered energies > 0.39 eV) ^3P ground state species. Furthermore, about 60% of the scattered ^3P species have velocities characteristic of a Maxwell-Boltzmann distribution at the surface temperature, suggesting that the O atom interaction with the silica surface is quite “strong” and leads to efficient energy transfer. These results are consistent with the observed very low ^1D survival probability and the apparent very efficient physical quenching of this species.

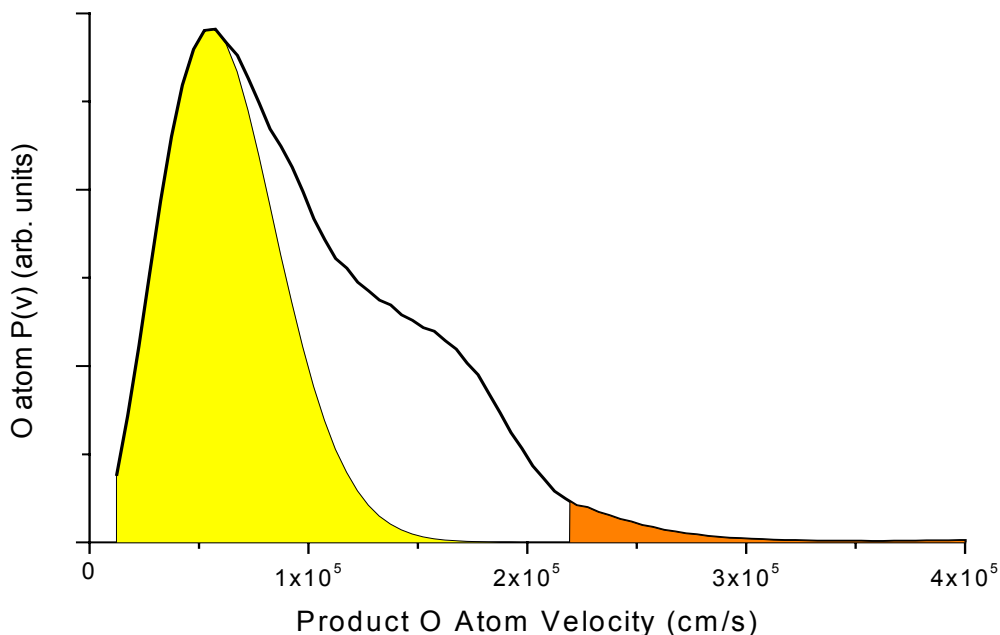


Figure 1. The bold line shows the velocity distribution derived from time-of-flight measurements of $\text{O}(^3\text{P})$ atoms scattered from fused silica. The portion of the distribution with velocities due to super-elastic species ($v \geq 2.2 \times 10^5$ cm/s) and those velocities characteristic of the surface temperature are indicated by the orange and yellow shaded regions, respectively.

Impact: The results of this work will soon be submitted for publication in the open literature. These results provide key information on the energy accommodation and survival coefficients of ground and metastable O atoms interacting with a fused silica surface. Since fused silica is widely used in the generation and containment regions of plasma reactors, it is anticipated that these results will significantly impact accurate modeling of oxygen plasma systems.

Future Plans: This activity focusing on O atom reactivity with fused silica is completed. The availability of resources as well as the relevance and experimental suitability of other surface systems are being evaluated.

Improvement of Value Assignments for NIST and IAEA Stable Isotope Reference Materials

CSTL Program: International Measurement Standards

Authors: *R.M. Verkouteren, and D.B. Klinedinst; M. Groening (IAEA)*

Abstract: Operational artifacts were recently discovered in isotope ratio mass spectrometers (IRMS). This prompted the International Atomic Energy Agency (IAEA) to convene a panel of experts to inspect the susceptible isotope metrology. One recommendation was a comparison exercise, led by NIST, of key isotope Reference Materials (RMs) designed to overcome the limitations of IRMS.

The intercomparison exercise was completed this year and data were processed through a standard algorithm (<http://www.nist.gov/widps-co2>). Results show significant shifts in most value assignments with up to 3-fold improvements in uncertainties over prior exercises.

International utilization of the NIST isotope RMs includes the Institute for Reference Materials and Measurements (IRMM) in Belgium, where the SI has been realized through NIST RMs 8562, 8563, and 8564. This traceability will give modelers of climate change more accurate information regarding the global carbon cycle. The National Institute for Environmental Studies (NIES) in Japan has used NIST RMs 8562 and 8564 to calibrate a specialized CO₂ standard for detailed studies of ocean-atmosphere exchange. Researchers at the Max-Planck Institute in Germany, under the European Network for Research in Global Climate Change, have utilized the NIST Web-based standard algorithm to verify the accuracy of isotopic measurements used for extremely precise analysis of atmospheric species.

Purpose: Subtle yet significant operational and data evaluation artifacts were recently discovered in modern isotope ratio mass spectrometers (IRMS). This prompted the International Atomic Energy Agency (IAEA) to convene a panel of technical experts to inspect the susceptible isotope metrology frameworks and to assess the impacts to the international isotope measurement communities and IAEA Member States. A recommendation from the panel was the reassessment of value assignments of ¹³C and ¹⁸O isotope Reference Materials (RMs) distributed by the IAEA and NIST. A comparison exercise, led by NIST, of key RMs was designed to overcome the inherent limitations of IRMS in order to substantially improve the accuracy and consistency of the RM value assignments.

Major Accomplishments: The intercomparison exercise was completed this year with the reporting of measurement data from Poland, Canada, and China. These data were merged with data from The Netherlands, Germany, Austria, and the United States, and were processed through a standard algorithm now available on a NIST web site (<http://www.nist.gov/widps-co2>). Results show significant shifts in most values and up to 3-fold improvements in uncertainties over prior exercises.

Impact: Interest from several international and U.S. industrial groups has been evident this year:

- Researchers at the Institute for Reference Materials and Measurements (IRMM) in Belgium have realized the SI through absolute IRMS of the three NIST CO₂ isotope RMs (RM 8562, RM 8563, RM 8564). These determinations of the absolute ratios of CO₂ isotopomers now give modelers of climate change more accurate information regarding the global carbon cycle.
- The National Institute for Environmental Studies (NIES) in Japan has used RM 8562 and RM 8564 to value assign a CO₂ Reference Material produced especially for ocean studies. This material has an oxygen isotopic signature very close to ocean water, and will be useful for detailed studies of ocean-atmosphere chemical exchange.
- Researchers at the Max-Planck Institute in Germany, under the European Network for Research in Global Climate Change (ENRICH, DG XII), have utilized the NIST Web-based data processing system to verify the accuracy of isotopic measurements used for extremely precise analysis of carbonaceous species in the atmosphere.

Future Plans: The task is completed, and our activities are being redirected towards problem-driven R&D although the core program will also evolve with new international needs. U.S. industry representatives at the *NIST-NOAA Workshop on Atmospheric Measures and Standards* identified the need to develop more precise methods for the accurate apportionment of carbonaceous source emissions. These methods included the development of SRMs/RMs that are representative (chemically and isotopically) of atmospheric PM samples. The ¹³C isotope RMs developed over the last several years will be a foundation for this application.

We anticipate certifying the ¹³C and ¹⁸O value assignments of key RMs, as well as developing natural gas standards and isotope dilution mass spectrometry (IDMS) for carbon certification in soils and PM. The natural gas standards and the IDMS development are now funded as SRM tasks.

Several international atmospheric monitoring networks and organizations (Asia-Pacific Network, CSIRO; INSTAAR/NOAA; AEROCARB; WMO) are searching for a solution to a long-standing measurement traceability problem. Biases in high-precision measurements of atmospheric CO₂, including isotopic composition, exist across these networks. While the NIST isotope standards have been helpful to researchers in these networks, there are further needs to improve the commutivity of these standards and the reproducibility of the CO₂-in-real air measurements. We are actively involved in international discussions to address these issues, which include the proposed GlobalHubs and BIPM/CCQM mechanisms.

Improved quantitative particle analysis using low-voltage electron beams

CSTL Program: Chemical Characterization of Materials

Author: *J.A. Small*

Abstract: Common to many industries associated with the high-technology sector of our economy is the need to quantitatively characterize nanometer and micrometer-sized particles. Particles are used in many critical components and products related to these industries such as feed stocks for thermal-barrier coating and hard-coating manufacturing and are critical to various product measurements for process control decisions such as product failure analysis. In the quantitative analysis of particles with electron-beam instruments, the size and shape of the particle often results in large analytical errors associated with x-ray emission and absorption. Over the years, several different researchers have developed correction procedures to minimize the uncertainties associated with particle analysis. Although these correction procedures reduce the effects of particle geometry, elemental concentrations determined from the quantitative analysis of particles by these methods are often accompanied by errors on the order of 10-50 % relative compared to 3-5 % relative errors for the analysis of conventional samples. (See figure 1.)

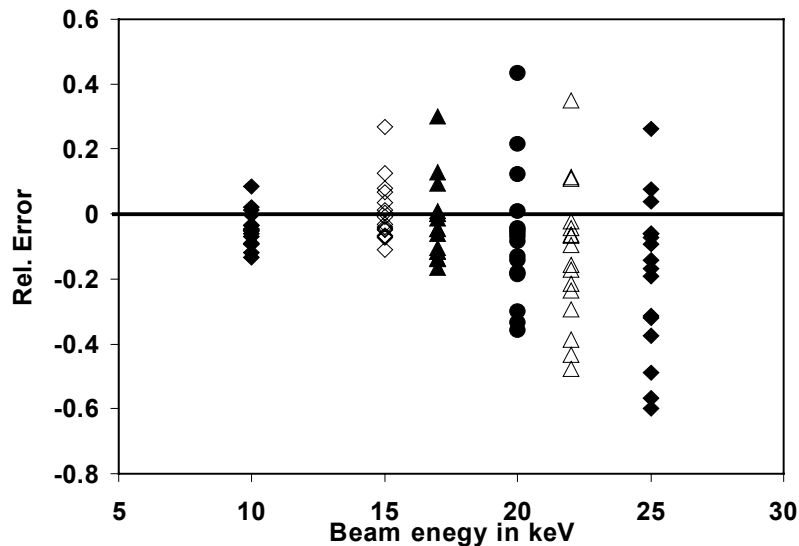


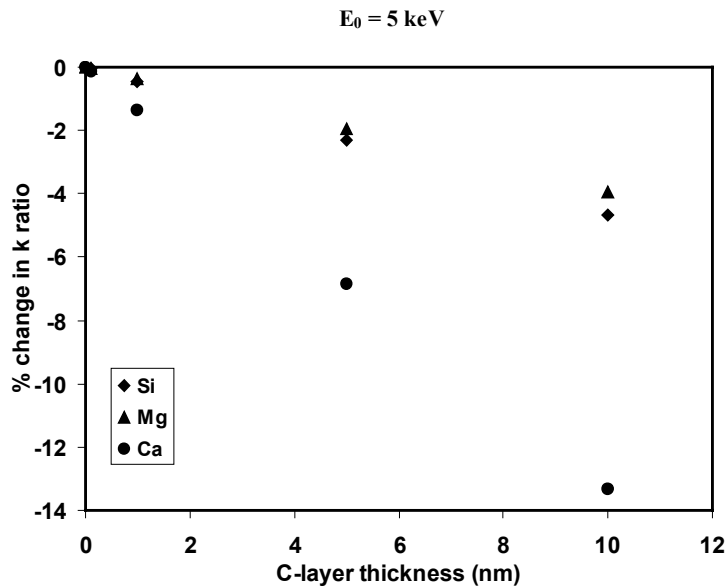
Figure 1. Plot of the relative errors for particle analyses vs. electron beam accelerating voltage.

The new generation field-emission electron beam instruments used in conjunction with new detector technologies like the NIST microcalorimeter x-ray detector may make it possible to use electron beam energies in the range of 3 keV to 10 keV to significantly reduce the analytical uncertainties associated with the quantitative analysis of particles.

We have demonstrated improved accuracy of quantitative results on particles by reducing the energy of the electron beam from 25 keV to 10 keV.

Purpose: The purpose of this work is to improve our ability to quantitatively analyze nanometer- and micrometer-sized particles. The primary customers are the analysts and process engineers in many industries associated with the high-technology sector of our economy for example, the semiconductor and advanced ceramics and metal powder industries and environmental monitoring industries that need to accurately characterize the chemical composition of particles.

Major Accomplishments: During this year we have initiated efforts to understand better the practical implications and potential limitations of applying low-voltage analysis to particles. Although the application of low-voltage analysis reduces the effects of particle size and shape it also introduces systematic errors in the analytical results that must be taken into account for accurate quantitative analysis. These errors are not related to particle geometry but are associated with the buildup of contamination under bombardment of the electron beam. The contamination lowers the intensity of the measured x-rays by lowering the average energy of the electron beam. This effect is particularly severe for elements that have x-ray excitation energies within 30 % of the electron beam energy as shown in figure 2 which is a plot of the percent change in x-ray intensity for Si, Mg and Ca in SRM 470 as a function of the thickness of a surface carbon layer.



Impact: Improving the quantitative analysis of particles will likely have a significant impact on expanding the application of microanalysis techniques to meet the future needs for increased resolution and speed in the analysis of nanotechnology systems, environmental particle populations, and HTE methods applied to materials science.

Future Plans: Our future plans for this program are to investigate ways to minimize the effects of contamination buildup associated with the low-voltage analysis of particles by modifying sample preparation procedures and employing high-vacuum instruments. In addition we plan to develop new quantitative procedures for particle analysis based on low-voltage electron beam excitation.

Development of an International Standard for the Evaluation of Microheterogeneity of Reference Materials for Microanalysis

CSTL Program: International Measurement Standards

Authors: *R.B. Marinenko; S. Leigh (Statistical Engineering Division), and M. Styles (British Standards Institute)*

Abstract: An ISO document titled *Microbeam analysis - Electron probe microanalysis - Guide to specification of certified reference materials (CRMs) ISO/CD 14595* was written to provide guideline procedures for the evaluation of candidate specimens as microanalysis reference materials for electron probe microanalysis (EPMA) and other microanalytical techniques. The document details the physical and chemical requirements of an EPMA reference material and provides procedures for testing the extent of heterogeneity of each element in a material with EPMA.

With careful data acquisition, uncertainties due to the experimental x-ray counting statistics, to the between specimen heterogeneity, and to the within specimen microheterogeneity can be determined in mass fraction for each element tested. A spreadsheet that can be easily edited is included to facilitate the calculation of these uncertainties. This document will provide guidelines for any laboratory that requires accurate quantitative microanalysis such as high-technology industries where reference materials are important in determining the accurate composition of materials such as ceramics, semiconductors, or metal oxides, and in the mining, geology and mineralogy communities where accurate evaluation of element compositions is needed. This document will also be useful to those with contract requirements specifying verification or traceability of reference materials. A version of the document has been prepared for publication; it is presently in the NIST review process before submission to a journal.

Purpose: This document was prepared to provide guideline procedures for the evaluation of candidate specimens as microanalysis reference materials for electron probe microanalysis (EPMA) and possibly other microanalytical techniques. Although the procedures described in the document have to some extent been loosely followed in some parts of the microanalysis community in the past, a rigorous description of proper certification procedures has not heretofore been readily available to the microanalysis community. In fact, during the early stages of the preparation of this document, there was evidence of poor understanding and a general lack of rigor as to how to properly evaluate materials as reference materials for microanalysis. The primary beneficiaries of the document will be from all fields - industry, academia, and government - where accurate quantitative microanalysis is important in the development of products or the analysis of materials.

Major Accomplishments: R. Marinenko and S. Leigh (Statistical Engineering Division) of NIST prepared an ISO document titled *Microbeam analysis - Electron probe microanalysis - Guide to specification of certified reference materials (CRMs)* with M. Styles, representative of the British Standards Institute (BSI). Dr. Marinenko is presently convenor and an expert member with Dr. Styles on Working Group 1 of the ISO

(International Standards Organization) TC202 (Microbeam Analysis) SC2 (Electron Probe Microanalysis). This document pertains primarily to flat, polished, solid specimens that exhibit long-term stability under normal environmental conditions as well as to the impact of an energetic (5 kV to 30 kV) electron beams with currents of 20 nA to 100 nA. It details these and other chemical and physical characteristics that are required of good quality microanalysis standards, including a detailed description of how to test candidate reference materials for the extent of microheterogeneity of each element present within each specimen and between specimens. A nested statistical scheme as described in ISO Standard Guide 35 is used, but is expanded from bulk specimen to specimen comparisons to comparisons from micrometer to micrometer within each candidate specimen. The statistics developed for the document are a combination of procedures used during the past thirty-five years of development of NIST Standard Reference Materials for microanalysis, contributions from the National Physics Laboratory, UK, and suggestions from other county members of the WG2. From a well-designed sampling procedure including replicate x-ray count readings from a single point, analysis of several points per specimen, and consistent sampling from specimen to specimen, the user can determine the uncertainty in mass fraction due to specimen heterogeneity taking into account the measured experimental counting uncertainty. The between point and between specimen uncertainties can be specifically calculated in this procedure. Since uncertainties are in mass fraction, they can be combined with the uncertainties determined from a bulk quantitative analysis for certification.

Part of the document includes a spreadsheet for the heterogeneity testing. The spreadsheet can be easily edited by a new user, therefore avoiding the arduous task of calculating or programming the series of equations. A final version of the document was submitted to the ISO and is expected to have final approval as a DIS (International Standards Document) in December 2001.

Impact: This document should provide valuable guidelines to numerous laboratories that require accurate quantitative microanalysis such as the high-tech industry where reference materials are important in determining the accurate composition of materials such as ceramics, semiconductors, or metal oxides, or in the geology and mineralogy communities where accurate evaluation of the compositions is needed. The document will be valuable to those with contract requirements specifying verification or traceability of reference materials.

Future Plans: Some minor corrections will be made to the spreadsheet when ISO will permit modifications. We also hope to finish the automation of the spreadsheet with NPL to further simplify the statistical evaluation of the data. A web based evaluation form is planned to enable easy access and implementation of the standard.

Certification of SRM-2241: Raman Intensity Standard

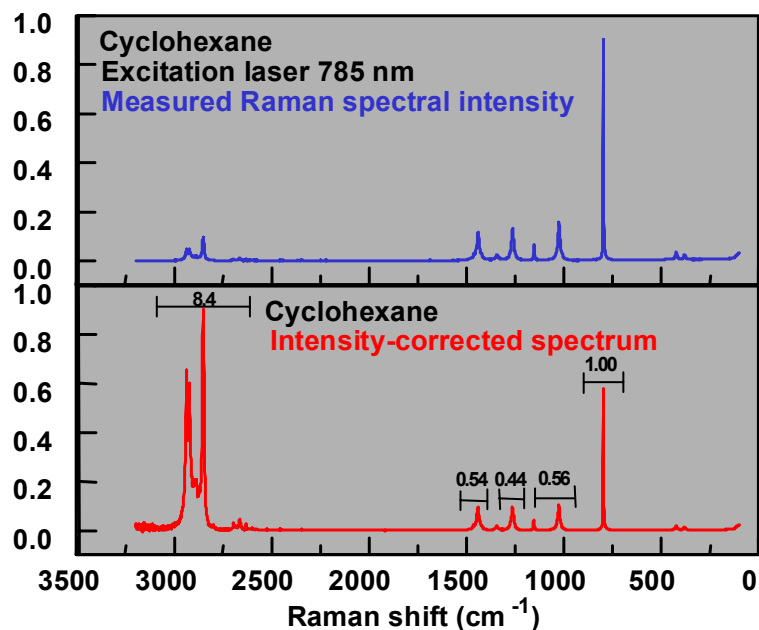
CSTL Program: Chemical Characterization of Materials

Authors: *E.S. Etz; W.S. Hurst (836), S.J. Choquette (839), and D.H. Blackburn (Contractor)*

Abstract: The first of a series of Standard Reference Materials (SRMs) for the correction of the Raman spectral intensity has been prepared for issue in FY2002. SRM-2241 consists of a fluorescent glass developed for the calibration of the spectral response function of Raman spectrometers when used with 785 nm laser excitation. SRM-2241 is a chromium-doped silicate glass that emits a broad, featureless fluorescence spectrum when excited with 785 nm radiation. The certification of this SRM entails a polynomial equation that describes the shape of the fluorescence spectrum. This mathematical function is used in the numerical correction of the observed Raman band intensities. In this spectral calibration procedure, the luminous output of the glass is traceable to a NIST primary radiometric standard. Thereby, a white light calibration of the Raman intensity is transferred to the sample spectrum through the measured fluorescence of the SRM glass.

Purpose: Recent advances in analytical Raman instrumentation have revolutionized Raman spectroscopic measurements. A variety of Raman spectroscopy techniques have now established themselves in the industrial environment for process measurements and quality control. These developments have fostered the recognition of a general lack of accepted practices, standards, and spectral libraries that would assure a well positioned role of Raman

spectroscopy in the industrial setting, especially in the regulated industries. While the calibration of the Raman frequency (or Raman shift, cm^{-1}) is comparatively well in hand through an existing ASTM standard, the calibration of the Raman intensity is not. Intensity calibration of Raman spectra can be accomplished with white light sources, but this procedure has many drawbacks and provides numerous pitfalls. These practical limitations are avoided by the approach adopted by NIST to provide a means for the calibration of the Raman intensity through the use of fluorescent glasses with spectra of known relative irradiance. The development of SRM-2241 has been closely coordinated with the Raman community, involving major chemical industries, instrument manufacturers, and the regulatory agencies. Close coordination on NIST Raman standards activities has been set up with ASTM E13.08 Subcommittee on Raman Spectroscopy which has led this year to the conduct of a round-robin involving the measurement and evaluation of the candidate SRM glass.



Major Accomplishments: A chromium-doped silicate glass, with a broad-band fluorescence spectrum extending over the full Raman range, has been developed as a standard for the calibration of the relative Raman intensity in work with 785 nm laser excitation. This standard will be issued as SRM-2241 and its spectral characteristics and function have been characterized on three different Raman systems. The measurements leading to the certification of this SRM have addressed a number of experimental variables that are known to have a direct bearing on the use of this standard by the user community. Among the factors that govern the performance and validity of this standard are the laser irradiance conditions employed, specific aspects of the optical excitation and collection system, and variations of the spectral response of the luminescent glass to changes in ambient temperature and departures from the exact (785 nm) laser wavelength. The certification of this SRM entails a polynomial that describes the luminescence spectrum of the glass and which, through numerical calculations, corrects the observed Raman intensities to the true relative Raman intensities. The uncertainties associated with these measurement and computational procedures determine the accuracy of the intensity correction. For this SRM, the relative uncertainties in the corrected intensity are well within 10 percent across the full Raman spectral range. The Raman spectra shown in above are those of the observed (a) and the intensity corrected (b) spectrum of cyclohexane, obtained through the calibration procedures of SRM-2241. The true Raman intensities are established through the calculation of the relative band intensity ratios.

Impact: The availability of NIST SRMs for the calibration of the Raman intensity represents an important step toward providing the analytical Raman community with the practical means toward a standardized representation of Raman spectral data. This will promote the acceptance of Raman methods and provide for instrument qualification as required by regulatory agencies.

Future Plans: NIST intends to issue a series of Raman intensity SRMs for work at other principal laser wavelengths. The next two SRMs of this type were determined in consultation with ASTM E13.08, representing the user community, and are the standards for 532 and 1064 nm work. For these SRMs, suitable doped-glass compositions have been identified to furnish the required luminescence properties. These candidate glasses are presently examined for stability, resistance to photobleaching, and homogeneity of composition.

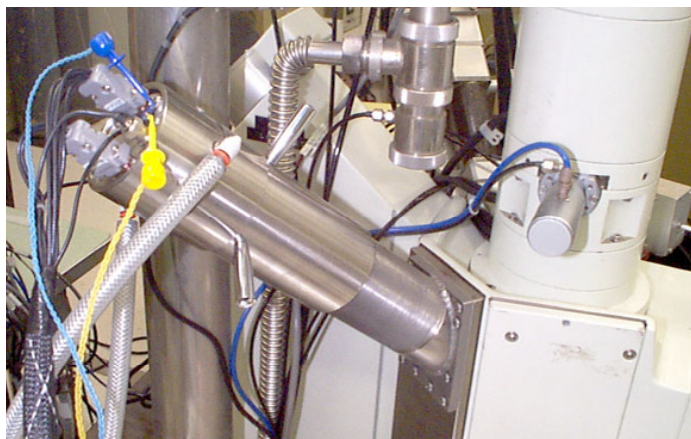
Silicon Drift Detector for Rapid X-ray Spectrometric Analysis

CSTL Program: Chemical Characterization of Materials

Authors: *D.E. Newbury, and J.A. Small; J. Iwanczyk, and S. Barcan (Photon Imaging, Inc. Los Angeles, CA)*

Abstract: X-ray spectrometric analysis is a basic tool for materials characterization and process control. Current technology offers a stark choice between energy dispersive spectrometry (EDS) coverage (0.1 to 20 keV or higher) but at low total spectrum count rate (~25 kHz) and high count rate (100 kHz or more) wavelength dispersive spectrometry (WDS) but with a narrow energy band pass (0.010 keV). A silicon drift detector (SDD), a new semiconductor x-ray detector technology capable of EDS operation at several hundred thousand counts per second, could revolutionize microanalysis applications. The new technology of the SDD consists of a carefully shaped charge collection field that is imposed by a photolithographically applied

electrode pattern on the back surface of a thin large area Si wafer. Combined with higher operating temperature to increase the drift velocities of the charge carriers, smaller thickness dimension to reduce drift distance, and a much smaller collection anode, the SDD produces much shorter pulses that yield much higher counting rates. The upper limit of a conventional Si-EDS is about 25



kHz with 175 eV resolution, whereas the SDD produces pulses compatible with 500 kHz counting. Division 837 researchers are working in cooperation with Photon Imaging to characterize the SDD in an SEM environment.

Purpose: To develop a new class of high count rate x-ray spectrometer, the silicon drift detector, which will benefit a wide range of applications in materials characterization (e.g., scanning electron microscope, analytical electron microscope) and process control (e.g., x-ray fluorescence, x-ray diffraction).

Major accomplishment:

X-ray spectrometric analysis is a basic tool for materials characterization and process control. Current technology offers a stark choice between energy dispersive spectrometry (EDS) coverage (0.1 to 20 keV or higher) but at low total spectrum count rate (~25 kHz) and high count rate (100 kHz or more) wavelength dispersive spectrometry (WDS) but with a narrow energy band pass (0.010 keV). As a result of an NIST Small Business Innovative Research (SBIR) Phase II grant, Photon Imaging, Inc. of Los Angeles, CA has developed a silicon drift detector (SDD), a new technology semiconductor x-ray detector capable of EDS operation at several hundred thousand counts per second. Like the

conventional large crystal Si-EDS, the SDD measures x-rays by photoelectric capture and charge deposition through free electron-hole pair formation during inelastic scattering of the photoelectron. The new technology of the SDD consists of a carefully shaped charge collection field that is imposed by a photolithographically applied electrode pattern on the back surface of a thin large area (50 mm²) Si wafer. Combined with higher operating temperature (~230 K vs. ~80 K) to increase the drift velocities of the charge carriers, smaller thickness dimension (300 μm vs. 3 mm) to reduce drift distance, and a much smaller collection anode (0.01 mm² vs. 50 mm² for an equivalent detector area), the PI SDD creates much faster pulses that yield much higher counting rates. The upper limit of a conventional Si-EDS is about 25 kHz with 175 eV resolution, whereas the SDD produces pulses compatible with 500 kHz counting. NIST researchers are working in cooperation with Photon Imaging to characterize the SDD in an SEM environment. Indeed, experiments at NIST have demonstrated output count rates from the SDD in excess of 1 MHz, far greater than the performance of existing pulse binning systems. Digital pulse processing is being investigated to overcome these limitations.

During FY2001, Division 837 implemented a 50 mm² silicon drift detector with 165 eV resolution (FWHM at MnK α) on a scanning electron microscope and characterized its performance envelope.

Impact: This is a newly developed detector with potentially enormous impact to reinvigorate the U.S. EDS industry, but the project ends with Phase II. The SBIR Phase III leads to commercialization, but the NIST/DoC SBIR program does not have resources to fund Phase III.

Future Plans: NIST scientists will continue to work with Photon Imaging, Inc. and other companies to overcome the limitations encountered in processing spectra at speeds consistent with the performance of the detector.

Chemical Imaging of Thin Film Polymer Blends with Near-Field Infrared Microscopy and Spectroscopy

CSTL Programs: Chemical Characterization of Materials, and Nanotechnology

Authors: C.A. Michaels, and S.J. Stranick; D.B.Chase (DuPont Co.)

Abstract: Infrared (IR) near-field scanning optical microscopy (NSOM) has been used to study nanoscale spatial variations in chemical composition for a series of thin film organic systems of interest to members of the NIST/industry polymer interface consortium. Characterization of lateral phase segregation in the polystyrene (PS)/polyethylacrylate (PEA) system by near-field spectral imaging on the aromatic C-H stretching band of PS has been completed, with spatial resolution (~ 400 nm) well below the diffraction limit. PS microspheres dispersed in a polymethyl methacrylate (PMMA) matrix have been studied with IR near-field microscopy. The microspheres can be clearly differentiated from the PMMA based on absorbance due to the distinctive aromatic C-H stretching vibration of PS. The relative importance of refractive and absorptive contrast in near-field IR imaging has also been investigated. Future efforts will include the use of apertureless near-field probes for the purpose of improving the attainable spatial resolution and expanding the accessible range of imaging wavelengths.

Purpose: To study nanoscale spatial variations in chemical composition for a series of thin organic film systems using an NSOM that incorporates IR absorption as an optical contrast mechanism, thus coupling the high spatial resolution of scanning probe microscopy with the chemical specificity of vibrational spectroscopy. The near-field spectral images are used to benchmark the chemical imaging capabilities of this microscope on samples of interest to our collaborators in the NIST/industry consortium on the *Characterization and Modeling of the Interfaces and Interphases of Polymeric Materials and Systems*. Analysis of these images also allows for the identification and characterization of sources of near-field image contrast, including scattering and infrared absorption, necessary for meaningful image interpretation.

Major Accomplishments: Polymer blend films investigated include PS/PEA and PS/polyacrylic acid (PAA), both model systems for the study of degradation and corrosion of organic coatings on metal surfaces. Characterization of lateral phase segregation in these systems by near-field spectral imaging on the aromatic C-H stretching band of PS has been completed. Fig. 1 shows the IR absorbance spectra of PS (solid line) and PEA (dashed line) in the CH stretching region along with the spectrum of the broadband IR laser (gray) tuned to the

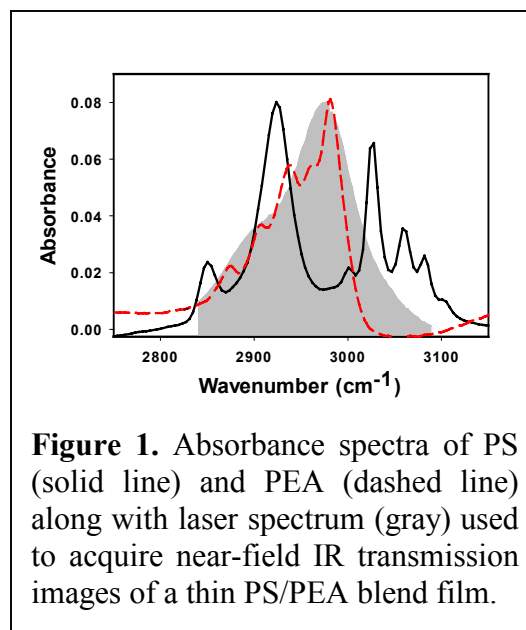


Figure 1. Absorbance spectra of PS (solid line) and PEA (dashed line) along with laser spectrum (gray) used to acquire near-field IR transmission images of a thin PS/PEA blend film.

center wavelength ($\lambda = 3.36 \mu\text{m}$) used to acquire this data. The obvious differences in absorbance over this spectral region, including distinct bands of PS absorbance (3025 cm^{-1}) and PEA absorbance (2980 cm^{-1}), allow for the differentiation of these two materials with spatial resolution ($\sim 400 \text{ nm}$) well below the diffraction limit. Fig. 2 shows an $8 \times 8 \mu\text{m}$ near-field spectral image frame of the PS/PEA film acquired at 2980 cm^{-1} . Analysis of the spatial and spectral variations in near-field transmission contrast over many image frames, such as that shown in Fig. 2, allows for the identification of the minority phase (bright features in Fig. 2) composition as being PS rich, in agreement with the results of a selective etching/ AFM analysis of a similar sample. This identification rests on the capability of this microscope to measure the differential absorbance due to a PS feature having only a nominal lateral size of $1 \mu\text{m}^2$ and a thickness of 500 nm . The broadband nature of the light source also allows for the robust analysis of the relative importance of scattering and absorption as sources of near-field image contrast. Near-field spectral images of PS microspheres dispersed in a PMMA matrix were also acquired to demonstrate the analytical capabilities of this technique. The PS particles can be clearly differentiated from the PMMA based on absorbance due to the distinctive aromatic C-H stretching vibration of PS, with sub-wavelength spatial resolution.



Figure 2. $8 \times 8 \mu\text{m}$ near-field transmission image of PS/PEA blend film acquired at 2980 cm^{-1} . Based on the spectral variation in near-field image contrast, the high transmission features are identified as being PS rich.

Impact: A manuscript describing the work on the PS/PEA system has been submitted for a special issue of *Vibrational Spectroscopy*. The application of this technique to the study of thin film organic systems has been also been reported at a number of industrial visits and meetings, including those with our collaborators in the polymer interface consortium. Additionally, efforts to facilitate the transfer of near-field chemical imaging technology to industrial partners through sample evaluation and interaction with guest scientists are ongoing.

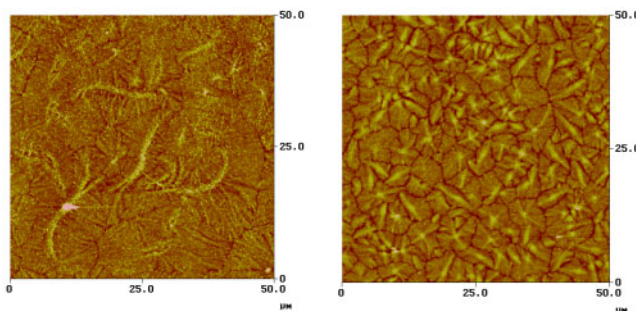
Future Plans: Application of this nanoscale chemical imaging technique to new sample systems of interest to our industrial collaborators will continue, as will efforts to extend our quantitative understanding of near-field image contrast in the infrared spectral region. Instrumental development efforts will focus on the use of evanescent or apertureless probes as a means of achieving high spatial confinement of the infrared radiation, leading to further improvements in spatial resolution. The inherent broadband nature of this approach will also be exploited to broaden the range of materials amenable to study with near-field IR imaging.

Combinatorial Measurements of Nucleated Crystallization in Polypropylene Films

CSTL Program: Chemical Characterization of Materials

Authors: *M.L. Walker; A.P. Smith (844), and Alamgir Karim (854)*

Abstract: The degree of crystallization and regularity of crystallite size have noticeable effects on properties of bulk polypropylene. The effects of these parameters, however, have not been well characterized in thin films. Control of crystallization and crystallite size could impart unique properties to thin polypropylene films. Isotactic polypropylene ($M_W = 190,000$, $M_N = 50000$) was dissolved in hot solvent (xylenes) with and without the nucleating agent 4-biphenyl carboxylic acid, and subsequently flow-coated onto heated silicon substrates to create thin films with continuous thickness gradients between 50 nm and 150 nm. Optical microscopy and tapping mode atomic force microscopy were used to explore combinatorially the effect of undercooling temperature, film thickness, and nucleating agent on crystallite size, regularity, melting behavior, and the extent of crystallization in these thin films. The presence of the nucleating agent in films does influence film behavior, substantially altering the crystallization process in these films as compared to films in which the agent is absent.



AFM images of the polypropylene films with (left) and without (right) the nucleating agent 4-biphenyl carboxylic acid.

Purpose: Understanding and subsequently improving the properties of polypropylene thin films is critical to both current and future applications. Polypropylene is the second most-widely used polymer worldwide behind polyethylene. It is used as a packaging material for food and beverage containers, automotive parts, and eventually may be used as thin sensory membranes found in microphones, motion sensors, and medical diagnostic devices. The properties of thin polypropylene films cast from solvent-based solutions of polypropylene containing added nucleating agents (at low concentrations of around 2% by weight to the amount of polypropylene in the solution) such as 4-biphenyl carboxylic acid are characterized using combinatorial/high-throughput methods. These properties, including the extent of crystallinity and the onset of crystallite formation as a function of film thickness, temperature, and nucleating agent, have not been systematically characterized previously in thin films.

Major Accomplishments: Thin polypropylene films, with and without the nucleating agent 4-biphenyl carboxylic acid, have been successfully cast on a heated stage with the film thickness varying linearly from approximately 50 nm to 150 nm. The morphology of films cast that were devoid of nucleating agent was determined by AFM and optical microscopy measurements. These resemble classic textbook images of crystallite

formation in polypropylene. These findings differed greatly from the morphology of the films containing the nucleating agent, which appeared to have extensive structure and less well-defined but larger crystallite structure. The lamellae are oriented perpendicular to the fibrils formed by the nucleating agent (Figure 1, top) and were seen throughout the entire thickness range of 50 to 150 nm. The polypropylene used in this study was determined by differential scanning calorimetry to have a bulk crystallization temperature of approximately 120°C. Upon annealing, the film samples were placed on a stage that had a linear temperature gradient from 100°C to 170°C. Polypropylene film (without the nucleating agent) began to crystallize at a temperature lower than 125°C (not shown), but the film containing the nucleating agent crystallized at temperatures as high as 145°C (Figure 2). These findings are consistent with the expected action of nucleating agents in the bulk. Clearly, the appropriate use of nucleating agents can affect processing temperatures and perhaps other parameters.

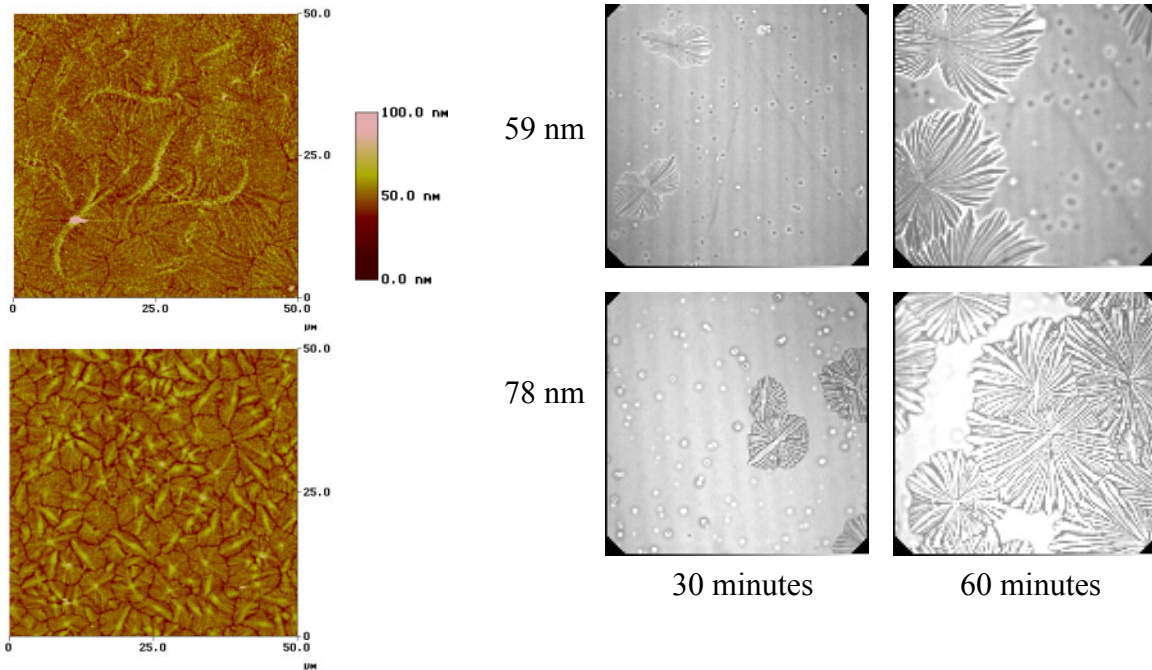


Figure 1. AFM images of polypropylene films with (top) and without (bottom) the nucleating agent 4-biphenyl carboxylic acid prior to annealing. Film thickness ~80 nm.

Figure 2. Optical micrographs (field-of-view ~ 290 µm) of the progression of crystallization for two polypropylene film thicknesses containing 4-biphenyl carboxylic acid at 145 °C.

Impact: These results help to demonstrate the utility of combinatorial methods applied to polymer/material science. The techniques developed here illustrate the breadth of information that can be obtained using a single gradient-based sample. This approach not only dramatically decreases the time required for sample preparation and evaluation, but also reduces measurement (e.g., sample-to-sample) errors and more effectively probes parameter space. This work highlighting the effects of nucleating agents on thin film polypropylene crystallization will be published in the open literature.

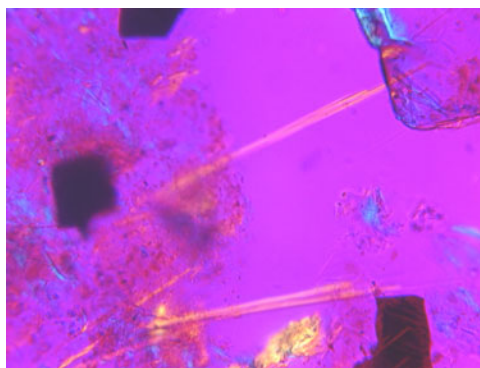
Future Plans: Studies involving the characterization of thin polypropylene films will continue, with emphasis on the variation of surface morphology and crystallite behavior with nucleating agent concentration and nucleation type. In addition, the kinetics of crystallization will be evaluated to further characterize the role of nucleating agents in the behavior of polypropylene thin films.

Asbestos Standards for Industrial and Environmental Contaminants

CSTL Program: Environmental Measurements

Author: *J.R. Verkouteren*

Abstract: SRM 1867a containing actinolite, tremolite, and anthophyllite asbestos will be reissued in FY2002. These materials serve as standards for the identification of asbestos by polarized light microscopy and are required for laboratories pursuing accreditation under the National Voluntary Laboratory Accreditation Program (NVLAP). The types of asbestos found in SRM 1867a are uncommon in commercial asbestos products, but are found as contaminants of some industrial minerals and in environmental settings. Increased scrutiny of materials for asbestos contamination has followed the recognition of severe, asbestos-related health problems in Libby, Montana. This standard improves the quality of asbestos analyses and thereby protects the public health and safety. The producers and users of industrial minerals benefit from improved accuracy in the identification of asbestos in the reduction of false positive results.



Polarized Optical Micrograph of Asbestos
SRM in vermiculite matrix

Purpose: Standards for the identification of asbestos by polarized light microscopy are required under the National Voluntary Laboratory Accreditation Program (NVLAP) for bulk asbestos analysis. The NVLAP for bulk asbestos, for which CSTL provides technical oversight, was initiated in response to the required evaluation of school materials for asbestos. SRM 1867, Uncommon Commercial Asbestos, was depleted in 2000 and a reissue was required. Recent events have made the reissue even more critical, as the types of asbestos present in SRM 1867 are under intense scrutiny following the health crisis in Libby, Montana. Actinolite, tremolite, and anthophyllite asbestos, although rare in commercial asbestos products, are more widespread in the environment and can be found as contaminants in industrial minerals, such as the vermiculite mined in Libby. Increased evaluation of asbestos contamination in industrial minerals and their products, and in environmental sources such as soils, has highlighted the need for a rapid reissue of this standard.

Major Accomplishments: The preparation of the standard and all measurements leading to the certification of SRM 1867a were completed during FY2001. Additional

measurements were performed to provide information values on the identification and concentration of other mineral phases, and the unit cell parameters of each asbestos type. The information values anticipate the use of the materials for calibration of other methods in addition to their primary use for optical microscopy. In addition, asbestos from Libby, Montana was characterized for optical properties and composition and sent to laboratories enrolled in the NVLAP program. A comparison of the properties of this material to those of actinolite asbestos in SRM 1867 was given to the participating laboratories.

Impact: The reissue of SRM 1867 serves the continuing purpose of protecting the public safety by promoting quality in asbestos analysis. The producers and users of industrial minerals benefit from improved accuracy in the identification of asbestos in the reduction of false positive results.

Future Plans: This activity is completed pending the final preparation and approval of the certificate. Potential new activity in this area includes method development for quantitative analysis of low concentrations (< 0.01 mass fraction) of asbestos in industrial minerals.

Verification of Calibration Procedure for Testing Military Gas Masks

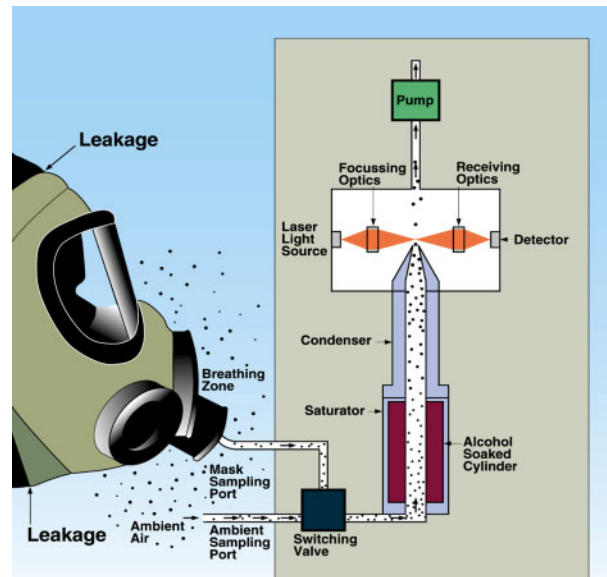
CSTL Programs: Environmental Measurements, and Nanotechnology

Authors: *R.Fletcher, R.L.King, and J.Small; M.Winchester (839); J.Yang, and G. Mulholland (866)*

Abstract: Military personnel wear gas masks for protection against a chemical and biological assault. The recognized potential global threat from chemical and biological agents demands that effective defense measures be taken. An important part of this defense strategy is the testing and verification that assures secure gas mask fits. The M41

system was developed for the military to field-test its protective equipment on the person using the protective devices. The Army determines the gas mask fit quality by measurement and comparison of the ambient aerosol concentration outside of the fitted masks to the aerosol concentration inside. The particles can identify both leaks in the mask and inefficiencies in the filters.

The objective of our research is to provide verification and possible development of a standard method that will allow the accurate calibration of Condensation Particle Counters that are currently used to calibrate the M41 Protective



Assessment Test Systems (PATS) for the Army. This goal will be achieved by a primary particle counting approach using electron microscopy and a secondary approach of determining the particle concentration in terms of electrical current using an aerosol electrometer.

Purpose: The objective is to provide measurement assurance to the U.S. Army for their gas mask fit-test method by verifying the accuracy of the aerosol concentration measurement integral to this test method. The Army, working with TSI, Inc., an aerosol instrument manufacturer, has developed the M41 Protective Assessment Test Systems (PATS) to test and verify the goodness of fit for the gas mask on the individual person that is issued the device. The M41s are tested and verified by the U.S. Army Test, Measurement, and Diagnostic Group using a fit-test calibration stand (test stand). The components of the test stand are an aerosol generator, aerosol electrical charger, a mobility classifier to produce monodisperse 80 nm diameter aerosol, an aerosol dilution system and two condensation particle counters (CPCs). The test aerosol concentration range is 100-10,000 particles/cm.³ The CPCs serve as the calibrants in the test stand for the M41s. There are no aerosol concentration standards for the CPCs nor are there certified reference materials available for aerosol concentration standardization. The measurement process currently has no links or traceability to a standards granting organization. The U.S. Army Test, Measurement, and Diagnostic Equipment Activity

(USATA) requires the development of an aerosol concentration standard method, traceable to the National Institute of Standards and Technology.

Major Accomplishments: During the year we have acquired test equipment and assembled an aerosol test stand that will deliver 80 nm diameter aerosol for measurement by a CPC, an aerosol electrometer and by microscopy. We have finished approximately 60% of the calculations to simulate particle loss in the CPC. A method was developed to provide NIST traceable calibration of the aerosol electrometer and some preliminary scanning electron microscopy was done to understand the problems associated with count metrology of 80 nm particles.

Impact: This verification and possible development of a standard method would enable the accurate calibration of Condensation Particle Counters that are currently used to calibrate M41 Protective Assessment Test Systems (PATS) for the Army. The Army serves as the sole calibration agent for the tri-services.

Future Plans: The project is on going having completed the first year of a two-year effort.

Grazing Incidence X-Ray Photoemission Spectroscopy Measurements of Gate Dielectrics: Internal Calibration and Comparison with X-Ray and Neutron Scattering

CSTL Programs: Microelectronics, and Nanotechnology

Authors: *T.Jach; and E.Landree (AAAS/DoD)*

Abstract: Grazing Incidence X-Ray Photoemission Spectroscopy (GIXPS) has been employed successfully as a novel means to analyze the depth, density, and chemical composition of the ultrathin dielectric layers being researched for future semiconductor devices. Serious discrepancies exist among the traditional methods of measuring these layers below 10 nm thickness. An important consideration has therefore been a determination of the accuracy of this new method and its potential sources of error. Discrepancies may also exist because of differences between phenomenological and discrete (i.e. atomic) measurements. We have addressed the first question by studying the dependence of the results obtained from the GIXPS method on the accuracy of the physical parameters required as inputs. We are studying the second question by comparison with scattering measurements by short wavelength probes like x-rays and neutrons.

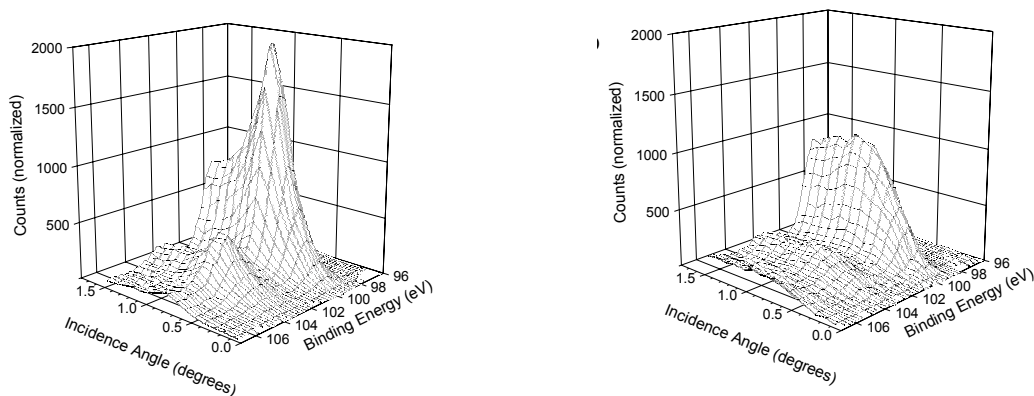


Figure 1. Comparison of Si 2p XPS spectra with angle taken at 1823 eV (left) and 1844 eV (right) from the same sample. The changes in the spectra reflect changes in the index of refraction across the Si K edge at 1839 eV.

Purpose: To meet its goal of semiconductor devices on a scale of 50 nm by 2003, the semiconductor microelectronics industry has projected the requirement of dielectric materials for transistor gates of no more than 2 nm thickness. While there are many methods such as ellipsometry, x-ray reflectivity, and TEM cross-sections used to measure the thickness of SiO₂ and more advanced dielectric films, a comparison between the methods indicates disagreements by as much as 50% below 5 nm. Most users continue to believe in the precision of their measurements, but as the absolute thickness of the films goes below this threshold, the value of the methods to guide future development comes into question. Most of the methods also depend on the input of physical parameters for

assumed chemical species that those methods cannot positively identify. The GIXPS method was developed to take advantage of many physical and chemical qualities of these layers at the same time (x-ray index of refraction, electron mean free path, chemical shifts between different species in photoemission). The idea is 1) to combine identification of the chemical species with sensitivity to thickness differences in very thin layers, and 2) to separate out the effects of thickness and density if possible. We have succeeded in demonstrating that the method provides both chemical and dimensional properties of gate dielectric layers. The next step is to determine how the results depend on the accuracy of the physical parameters used as inputs and to investigate the reasons for discrepancies with other measurements.

Major Accomplishments: We performed an analysis of the effects of errors in physical input parameters (e.g. x-ray cross-sections, atomic form factors, electron mean free paths) on the results obtained for films of different thicknesses. This allowed us to identify the sensitivity of the results to certain inputs. We were able to test one of these dependences experimentally on the tunable NIST beamline X-24A at the National Synchrotron Light Source. By performing the same photoemission experiment with x-rays of slightly different energies about the K excitation edge of Si, the physical performance of the same sample was dramatically changed. An extensive analysis showed that the two results for the same sample differed by 16%, which is a good indicator of the accuracy level of the optical parameters used in the determination.

We collaborated on measurements on high quality SiO₂/Si samples by x-ray reflectivity at high momentum transfer at the Advanced Photon Source. The Fourier inversion of the reflectivities yields electron density with depth. Similarly, we have measured the neutron reflectivity from the same samples on a cold neutron beamline at the NIST Reactor. We are in the process of extracting mass densities from the data with depth. These determinations allow us to calibrate the electron densities and mass densities used in layer thickness fits by GIXPS, which may differ greatly in thin films from the quoted values in the literature for bulk compounds. This type of verification has not been readily available.

Impact: We have reported on these results in invited talks at conferences largely attended by members of the semiconductor metrology industry. We have also presented the results in talks at semiconductor fabrication facilities. There is a great deal of concern over the inconsistency in different dielectric film thickness measurements and the need for new techniques. There have been many questions about the ability to move this technique to laboratory instruments.

Future Plans: This work will be extended in several directions. 1) We are investigating the physical nature of discrepancies among the different thickness measurement techniques. 2) We are collaborating on a test of GIXPS measurements made with a specially modified commercial x-ray photoemission instrument using monochromatized Al K radiation. 3) We intend to look at relative chemical shifts in photoemission with depth. 4) We would like to use GIXPS to investigate the chemical properties of new gate dielectric materials such as hafnium or zirconium oxides on Si.

High Precision Measurements of Arsenic and Phosphorous Implantation Dose in Silicon by Secondary Ion Mass Spectrometry

CSTL Program: Microelectronics

Authors: *P.H. Chi, and D.S. Simons; J.M. McKinley, F.A. Stevie, and C.N. Granger (Agere Systems)*

Abstract: The Metrology section of the 1999 International Technology Roadmap for Semiconductors (ITRS) specifies in-line dopant profile concentration precision requirements ranging from a value of 5 % in 1999 to a value of 2 % in 2008. These values are to be accomplished with “low systematic error”. Secondary ion mass spectrometry (SIMS) has demonstrated the capability to meet these requirements for B, As, and P. However, the detailed analytical protocols required to achieve these goals have not been completely specified. This project investigated the parameters that must be controlled to make highly repeatable dose measurements of As and P implants in Si with magnetic sector SIMS instruments. Instrument conditions that were investigated include analytical species, matrix ion species, energy bandpass, and sample holder design. With optimized settings, we demonstrated the ability to distinguish As or P implant doses differing by 5 %. High precision SIMS measurements of As and P concentrations in silicon are crucial for process control and new device fabrication in the US semiconductor industry. Secondary ion mass spectrometry is the primary tool used for these measurements. The analytical protocols developed in this work should be of widespread interest to the semiconductor industry

Purpose: Highly repeatable SIMS measurements are difficult to achieve for some elements, especially when the element of interest has a spectral interference with an element in the matrix. In this case, high mass resolution analysis or sample voltage offset is used to discriminate the molecular ion from the element of interest. In this study, six As-implanted Si and one P-implanted Si sample with implant doses ranging from 10^{14} cm⁻² to 10^{15} cm⁻² were depth-profiled along with SRM-2134, a Standard Reference Material for As dose and a prototype standard for P dose. The scope of this study is to identify artifacts that profoundly affect the measurement repeatability in SIMS, as well as to determine what protocol should work best to minimize the variability in the measurement.

Major Accomplishments:

Arsenic Implants

Six As-implanted Si samples were used in this study. The implants were in two groups, one with target doses of 0.95, 1.0, and 1.05×10^{14} cm⁻² and the other with target doses of 0.95, 1.0, and 1.05×10^{15} cm⁻². The measurement protocols included using the high precision sample holder, examining the sample flatness after each loading, analyzing only the central area on the sample, adjusting for a flat top peak on Si, and centering the energy window on the peak of the Si energy distribution. Three profiles were taken on each sample by monitoring $^{75}\text{As}^{28}\text{Si}^-$, $\text{Si}3^-$, and $\text{Si}4^-$ in low mass resolution mode. The calculated average As doses for the six samples measured over a three-month period are

1.4 % and 0.9 % average relative standard deviations for Si³⁻ and Si⁴⁻ matrix reference species, respectively. Results show the same dose ranking for two laboratories and this ranking agreed with the implant specifications.

Phosphorous Implants

All P profiles were measured in high mass resolution mode. The samples used in this study were a P-implanted Si at 100 keV with the consensus dose of $8.5 \times 10^{14} \text{ cm}^{-2}$ and another P-implanted Si sample at 130 keV with nominal implant dose of $1 \times 10^{15} \text{ cm}^{-2}$. These two samples were loaded in the same window in a high precision sample holder. We used similar procedures and protocols in the depth profiling of P as for the As measurement: high precision sample holder, centering the energy window on the peak of the Si energy distribution, and monitoring the P⁻ signal in an electron multiplier and the matrix Si in a Faraday cup. The relative sensitivity factor generated from the reference sample was used to calculate the doses for the unknown sample. The calculated average dose and standard deviation for the 130 keV P-implanted Si sample was $1.13 \times 10^{15} \pm 2.06 \times 10^{13} \text{ cm}^{-2}$. The RSD for the long-term measurement is less than 2%, which is slightly higher than the As measurement, but is still consistent with the international technology roadmap for semiconductors (ITRS) requirements.

Impact: High precision SIMS measurements of As and P concentrations in silicon are crucial for process control and new device fabrication in the US semiconductor industry. Secondary ion mass spectrometry is the primary tool used for these measurements. The analytical protocols developed in this work should be of widespread interest to the semiconductor industry.

Future Plans: Our future plan is to use these protocols in measuring ion implant dose on a routine basis as would be applied in a process control environment.

Mapping of Combinatorial Bio-Surface Test Substrates Using TOF-SIMS

Program: Chemical Characterization of Materials

Authors: *S.V. Roberson, and A.J. Fahey; A. Sehgal, and A.Karim (854)*

Abstract: Many types of new materials are being developed for use in bioreactors, tissue implants and drug delivery devices. To successfully introduce new products into the marketplace, it is imperative to rapidly identify the biocompatibility of candidate materials, particularly with the surface treatments adopted. Surface properties, such as surface free energy, are among the key issues influencing biocompatibility. We have developed a simple method for chemical modification of chlorosilane self-assembled monolayers (SAMS) on Si surfaces by exposure to a gradient of UV-ozone radiation to create stable substrates with a range of contact angles ($\theta_{\text{H}_2\text{O}} \approx 5^\circ - 95^\circ$) and surface energies on a single substrate. These gradient energy substrates are developed to potentially generate libraries for combinatorial studies of thin film phenomenology. The graded oxidation process presents a systematic variation of surface chemical composition. We have utilized contact angle measurements and time-of-flight secondary ion mass spectrometry (TOF-SIMS) to investigate this variation for a series of ions, among which are SiCH_3^+ , SiOH^+ and COOH^+ . We show that the macroscopic measurements of surface free energy/contact angle correlate with the detailed analysis of surface chemistry (as assessed by TOF-SIMS) on these test substrates.

Purpose: Combinatorial methods in chemistry and the pharmaceutical sciences have traditionally explored inorganic and organic synthesis of large collections (libraries) of compounds, which are then tested for particular physical and chemical properties. This technology has significantly increased the efficiency of drug and material discovery and necessitates the development of high-throughput screening/analysis techniques. The extension of combinatorial methods to materials science has resulted in a shift in emphasis from screening for “hits” and the design of molecular structures (as in drug discovery) to knowledge discovery obtained by rapidly exploring multivariable-parameter space and investigating how those variables (compositional, processing, etc.) affect phenomenological physics. Micro- and nanoscale patterning techniques are being used to generate libraries having a systematic variation of surface properties. These libraries provide multi-parameter spaces to study interfacial phenomena in thin films, adhesion and biocompatibility. Surface free energy is one property that we are exploiting in this work to create such libraries.

Major Accomplishments: A novel method of creating surface free energy gradients using UV-ozone (UVO) treatment has been developed. In the UVO photo-oxidation method, a surface is exposed to short-wavelength (184.9 nm and 253.7 nm) UV radiation. Molecular oxygen is dissociated by the 184.9 nm radiation and ozone by the 253.7 nm radiation. Atomic oxygen is simultaneously generated during these dissociations. We have utilized UVO exposure through variable density filters to generate silane monolayers with continuous free energy gradients. This treatment introduces a range of functionalities to the surface. Among these are carboxylate, carbonyl and other

oxygenated functionalities. The ensuing changes in free energy (as assessed in terms of surface wettability) that result from the addition of these polar functional groups were evaluated using contact angle measurements. We used time-of-flight secondary ion mass spectrometry (TOF-SIMS) to investigate the relationship between contact angle/surface free energy changes and the functional groups present on the surface of two different silane monolayers. TOF-SIMS is a surface analytical technique that is capable of detecting elemental and molecular species with a spatial resolution of $<1 \mu\text{m}$. Because of these characteristics, and the imaging capabilities of TOF-SIMS, the technique is ideal for compositional analysis of these and other combinatorial arrays.

Impact: Many types of new materials are being developed for use in bioreactors, tissue implants and drug delivery devices. To successfully introduce new products into the marketplace, it is imperative to rapidly identify the biocompatibility of candidate materials, particularly with the surface treatments adopted. Surface properties, such as surface free energy, are among the key issues influencing biocompatibility. We have developed a novel method for creating surface free energy gradients using UV-ozone (UVO) treatment of silane monolayers. The graded oxidation process resulted in surfaces with a systematic variation in surface chemical composition across the substrate which is characterized by TOF-SIMS. These compositionally variable samples may ultimately be used to rapidly assess the influence of surface composition on biocompatibility.

Future Plans: In future work, we will extend the graded oxidation process developed for SAM's to modification of poly (ϵ -caprolactone) polymer surfaces and utilize TOF-SIMS in a combinatorial assessment of biocompatibility. We will study the effect of surface energy on cellular reception from serum where all other conditions (soluble factors, seeding density, film preparation) are identical.

Accuracy of HRTEM gate dielectric film thickness measurements

CSTL Program: Nanotechnology

Author: *J.H.J. Scott*

Abstract: The ability of high-resolution transmission electron microscopy (HRTEM) to measure the thickness of sub-4 nm gate dielectric films is in question, pending a quantitative understanding of the errors and uncertainties in the measurement process. The goal of this work is to quantify the accuracy of HRTEM as a technique for measuring the thickness of such films. Because device performance is very sensitive to the dielectric thickness, semiconductor device manufacturers consider this a critical fabrication parameter and are keenly interested in its accurate measurement. To address this problem, a suite of computer modeling tools was developed to build virtual gate stacks and simulate HRTEM micrographs from these stacks (Figure 1). Using these new tools, several hundred images of amorphous SiO₂ films between Si substrates were calculated, covering a range of imaging conditions and sample parameters. Combining the apparent thickness from the micrograph (measured value) and the known thickness from the model (true value) calculation of the accuracy as a function of the input variables is possible. A quantitative understanding of the errors in HRTEM thickness measurements plays an important role in improving the quality and yield of semiconductor electronic device fabrication.

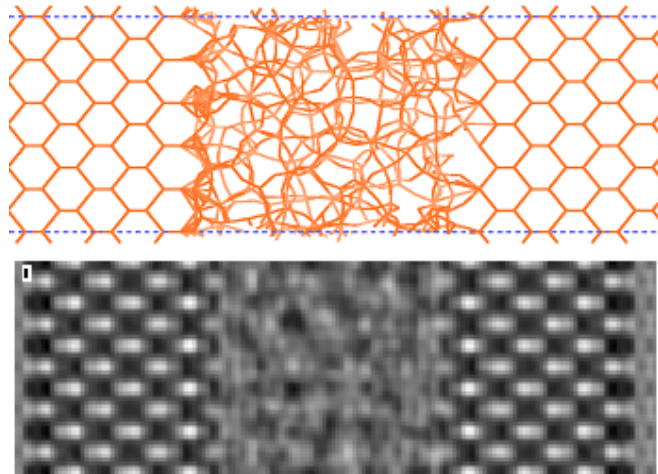


Figure 1. Molecular model of a gate stack (top) and one frame from an HRTEM simulation movie (bottom) showing changes in apparent thickness with changing imaging conditions.

Purpose: Fabrication tolerances for gate dielectric film thickness in semiconductor devices are approximately 0.2 nm. The performance of high-resolution (phase-contrast) transmission electron microscopy (HRTEM) at this level of performance is in question, pending a quantitative understanding of the errors and uncertainties in the measurement process. The goal of this work is to quantify the accuracy of HRTEM as a technique for measuring the thickness of ultrathin (< 4 nm) gate dielectric films. Because device performance is very sensitive to the dielectric thickness, semiconductor device manufacturers consider this a critical fabrication parameter and are keenly interested in its accurate measurement.

Major Accomplishments: A suite of computer modeling tools was developed to build virtual gate stacks and simulate HRTEM micrographs from these stacks (Figure 1). Using these new tools, several hundred images of amorphous SiO₂ films between Si substrates were calculated, covering a range of imaging conditions and sample parameters (Table 1). Combining the apparent thickness from the micrograph (measured value) and the known thickness from the model (true value) allows calculation of the accuracy as a function of the input variables. This revealed that measured thickness depends strongly on defocus and astigmatism. Using the Tcl scripting language, a graphical user interface was written to enhance the tools, improve efficiency, and simplify the database interface needed to manage the large amount of data that was generated.

Variable	Range
obj lens defocus	-70 nm to +30 nm
gate thickness	0.5 nm to 2.1 nm
spherical aberration	0.0 mm to 2.0 mm
tilt misalignment	0 mrad to 25 mrad
tilt azimuth	0° to 180°
astigmatism	0 nm to 30 nm
astigmatism azimuth	0° to 180°

Table 1. Major parameters varied during the simulations and their ranges.

Impact: These measurements provide a capability expressly requested by researchers at SEMATECH and semiconductor manufacturers. A quantitative understanding of the errors in HRTEM thickness measurements plays an important role in improving the quality and yield of semiconductor electronic device fabrication.

Future Plans: The project is currently limited by the inherently difficult task of extracting measured thicknesses from both experimental and simulated micrographs. Image processing tools are being developed to address this problem. Also, further characterization of the HRTEM imaging parameter space is in progress, with plans to map out the effects of along-beam thickness, amorphous thickness, and sample vibration on thickness measurements. Using statistical design of experiment (DOE) tools, the interrelationships between all of these factors can be determined.

Near-Field Microwave Microscopy For Materials Analysis

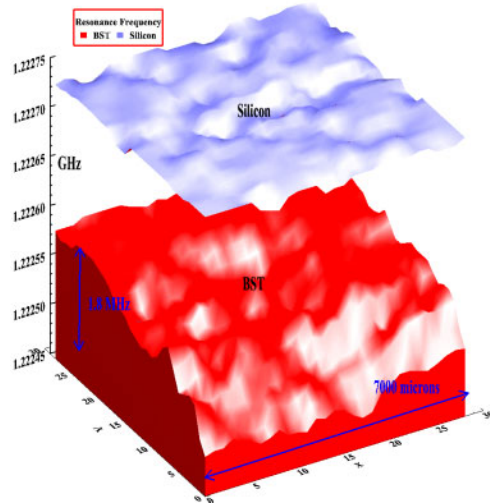
CSTL Programs: Nanotechnology, and Microelectronics

Authors: *S.J. Stranick, S.W. Robey, and C.A. Michaels; P.K. Schenck, and D.L. Kaiser (852)*

Abstract: We are developing robust microwave-frequency microscopy methodologies and data reduction strategies for dielectric imaging and high throughput screening of chemically textured arrays/libraries generated by combinatorial synthetic strategies. The work outlined in this report addresses issues regarding the maximum spatial resolution (smallest sample volume) and degree of accuracy (valid/factual information) that can be obtained with near-field microwave frequency microscopy. This new form of dielectric microscopy represents both a significant advance in the achievable spatial resolution and, more importantly, a dramatic increase in the speed at which dielectric characterizations can be made (higher throughput measurement).

Purpose: Common characteristics of advanced dielectric materials include high quality (defect free) homogeneous compositions that possess critical dimensions on short length scales (sub-micrometer). Given that these critical dimensions are well below that of the radiation wavelength, analysis by conventional dielectric probes, which look at materials on a macroscopic dimension, is no longer sufficient. Alternatively, a near-field microscope takes advantage of the non-propagating electromagnetic fields (evanescent fields) present at a sample's surface when exposed to an electromagnetic wave. This results in an improvement in the spatial resolution (below 100 nm). This resolution, unlike that of conventional dielectric probes, is largely wavelength independent. Additionally, the tip (a sharpened metallic probe) turns the non-propagating fields into radiation that can then be detected and analyzed.

Accomplishments: In our near-field microwave frequency microscope (microwave NSOM), microwave radiation up to 20 GHz is coupled evanescently to the sample surface using a sharp proximal probe that is part of a transmission line, resonant cavity structure. Analysis of reflected and



Dielectric response maps of a BST film gradient on a silicon substrate (Red) and of a bare silicon substrate (Blue).

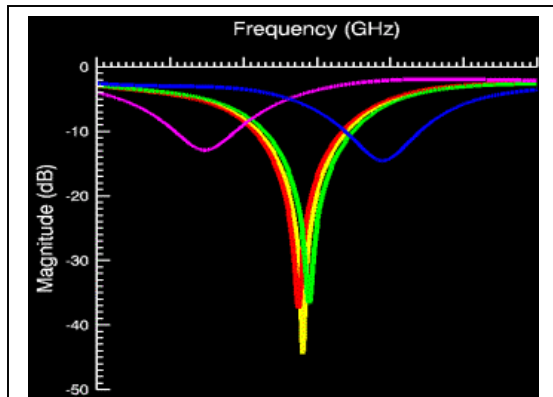


Figure 1. Shown are representative network analyzer measurements of one of the modes of the evanescent probe microscope's resonator.

transmitted signals is performed using a microwave frequency, vector network analyzer allowing the extraction of the dielectric properties of a material. The importance of going to microwave frequencies (2 to 20 GHz) is to gain access to information concerning the dielectric nature of materials at their intended operational frequency. Cavity and transmission line structures have been fabricated and evaluated for their ability to achieve maximum sensitivity and frequency agility. Shown in Figure 1 are representative single port, network analysis measurements of one of the modes of a probe resonator as it interacts with different regions of the sample. By monitoring the frequency of this resonance mode as the tip is scanned across the surface, a dielectric response map of a sample can be acquired. Such a dielectric mapping is shown in Figure 2. The sample under study is a thin-film dielectric coating of barium strontium titanate (BST) on silicon. The BST sample was fabricated by a dual-target pulsed laser deposition methodology. Using this sample preparation method, a compositional gradient is formed across the sample surface ranging from barium rich to strontium rich. More importantly, this results in a dielectric gradient; this is indicated by the frequency shift of the resonance mode of the cavity (Z axis of Figure 2). To correlate between frequency shift and dielectric constant, a range of samples of known dielectric responses were measured to calibrate the resulting frequency shift to a quantitative value of permittivity. Each of these samples is bulk in form and has a known dielectric response at the frequency of measurement. Given the detailed nature of the electric field distribution at the apex of an evanescent probe, it is often very difficult to determine *a priori* the electric field in or around the sample under study: the electric field is a critical parameter in determining the permittivity of a material. By measuring a series of known materials (Teflon: $\epsilon = 2.08$, MgO: $\epsilon = 10.0$, Sapphire: $\epsilon = 9.8$, Si: $\epsilon = 11.9$, SrTiO₃: $\epsilon = 300$, and LaAlO₃: $\epsilon = 24$) a calibration can be made and the field distribution in the near-field junction can be extracted.

Impact and Future Plans: The preliminary results outlined in this report are representative of the potential of a microwave evanescent probe microscope's to probe and determine the quantitative values of the dielectric response of small sample volumes. We are continuing to improve on both the sensitivity and speed in which these measurements can be made. Our current focus is on the total automation of data acquisition events, improved cavity structure designs, and implementation of

non-linear dielectric probes to further improve on our sensitivity at higher (>200) dielectric constants. Additionally, we are working on experimental protocols for the identification of measurement artifacts. At microwave frequencies, valid measurements

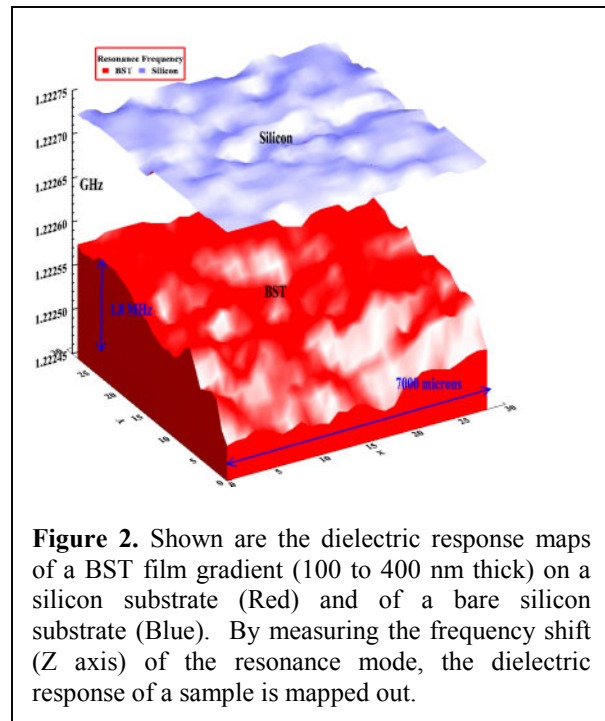


Figure 2. Shown are the dielectric response maps of a BST film gradient (100 to 400 nm thick) on a silicon substrate (Red) and of a bare silicon substrate (Blue). By measuring the frequency shift (Z axis) of the resonance mode, the dielectric response of a sample is mapped out.

of a dielectric response must take into account the effects of sample geometry, organic contamination, and resonant effects (the sample acting as a resonant structure) which can mask the true dielectric properties of a sample. These effects will be magnified when moving to smaller and smaller sample volumes as is the case with advanced materials/devices.

Selective study of molecular order at interfaces with vibrationally-resonant sum frequency generation via thin film interference effects

CSTL Program: Chemical Characterization of Materials

Authors: *P.T. Wilson, and L.J. Richter; K.A. Briggman, and J.C. Stephenson (844); W.E. Wallace (854)*

Abstract: We have developed a new technique that enables selective measurement of free and buried polymer interfaces by vibrationally resolved sum frequency generation spectroscopy (VR-SFG). This technique is generally applicable to optical quality films and is demonstrated here for the buried polystyrene/ dielectric interface. Manipulation of Fresnel coefficients through the choice of film thicknesses allows enhancement of the nonlinear optical signal from the desired interface and cancellation of the signal from other obscuring interfacial sources. Our spectra reveal intuitively and through straightforward analysis that the phenyl group orientation for the buried interface is in the opposite direction of the phenyl groups at the top surface. The molecular ordering at the polymer/dielectric interface changes with changing hydrophobicity of the dielectric surface and correlates to the adhesive strength of the interface.

Purpose: Surfaces and interfaces are critical to the functional properties of many polymer applications including the adhesion of polymer coatings for electronic packaging and optical fibers, biocompatibility of medical devices, the structural integrity of polymer composites and the formation of lamellae in block copolymers. Polymer interfaces can differ considerably from the bulk in important characteristics such as glass temperature, end-group concentration, molecular mass distribution, amorphous: crystalline ratio and crosslink density. Until recently, a technique to adequately characterize buried interfaces, and in particular, to determine the molecular structure at such an interface has been lacking. We have developed a novel system for non-linear optical spectroscopy to enable exploration of molecular structure at material surfaces and buried interfaces for a variety of applications.

Major Accomplishments: We previously determined the orientation of the pendant phenyl groups of polystyrene at the free surface of a thin film spin cast onto oxidized silicon wafers [J. Phys. Chem. B. 105, 2785 (2001)]. We have extended our studies to investigate the molecular structure of buried polymer interfaces, specifically, the polystyrene (PS) / spin-on-glass (SOG) interface. The thicknesses of the PS and SOG films are tailored to create optical interferences that enhance the signal coming from the interface of interest while attenuating the signal from other interfaces. The substrate is comprised of a hydrogen silsesquioxane inorganic polymer film spun and cured on a gold mirror. The untreated surface of a SOG thin film is terminated by silicon-hydrogen (Si-H) bonds, resulting in a low free energy, hydrophobic surface. Increasing exposures of this native SOG surface to UV activated oxygen species decreases the number of Si-H bonds in favor of silicon-hydroxyl (Si-OH) bonds, which form a high free energy, hydrophilic surface. Figure 1 shows the vibrationally resonant SFG spectra of the PS/SOG interface for a series of PS/SOG samples with varying exposure of the SOG substrate to UV activated oxygen (O_a). Analysis of the SFG spectrum of PS on the

untreated SOG substrate gives an absolute orientation of phenyl groups pointing away from the PS film with a tilt angle near 60° and a twist angle near 45° relative to the surface normal. This result is similar to that previously observed for the orientation of phenyl groups at the free PS interface. Changes in the SFG spectra for PS on the O_a treated SOG substrates correlate with changes in the tilt and twist angles of the pendant phenyl groups. The observed spectral changes suggest the phenyl groups lie more in the surface plane enabling favorable chemical interactions with surface Si-OH species. We are analyzing the subtleties of this orientational distribution to further understand this interaction.

The changes in molecular orientation observed with SFG were correlated with the adhesive strength of the polystyrene thin film/glass interface. A simple peel test is used to empirically measure adhesion of the PS films to the O_a -treated and untreated SOG substrates. PS films peel from the untreated, low surface energy, hydrophobic SOG substrates, but adhere to the O_a -treated, higher surface energy, hydrophilic SOG substrates.

Impact: We have demonstrated the use of a multilayer thin film stack to selectively measure the VR-SFG signal from buried interfaces through the manipulation of Fresnel factors. We expect this technique to be broadly applicable to polymer/polymer and polymer/dielectric interfaces. The study of molecular orientation at buried polymer interfaces and its influence on adhesion has been demonstrated. The influence of molecular orientation on the functional properties of a wide range of transparent media can now be explored.

Future Plans: We will explore the extension of this technique to characterization of polymer/metal interfaces such as electrolyte/electrode and electrolyte/catalyst interfaces in advanced fuel cells.

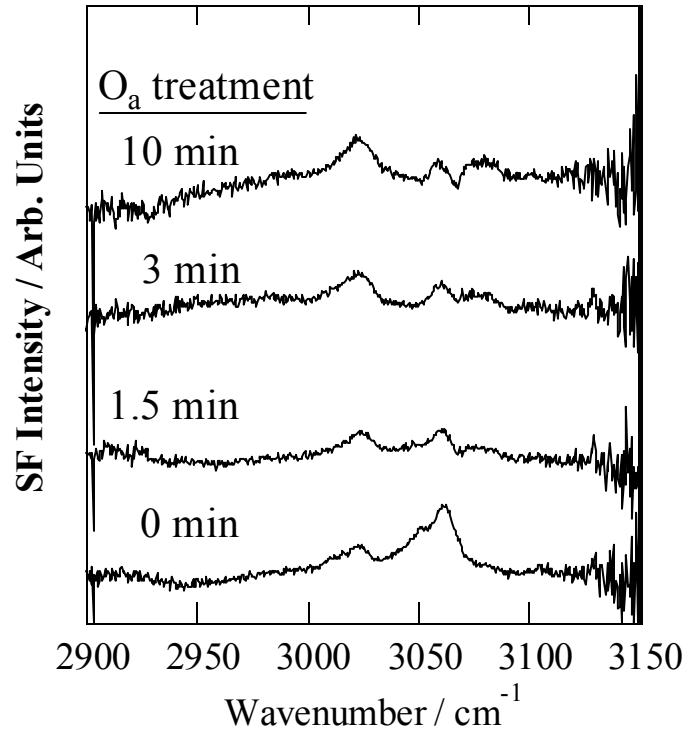


Figure 1. Vibrationally resonant SFG spectra illustrating changes in molecular orientation, which correlate with atomic oxygen treatment of the substrate and changes in adhesion

Production of SRM 2784: Filter-Based Fine Particulate Material

CSTL Program: Environmental Measurements

Authors: G.A. Klouda; J.J. Filliben (898), H.J. Parish (SRI International), and J.C. Chow (Desert Research Institute)

Abstract: SRM 2784 urban dust on quartz-fiber filter will be a Standard Reference Material designed for the evaluation of analytical methods used to characterize the carbon composition of atmospheric fine particulate matter (PM_{2.5}, having diameters nominally less than 2.5 micrometers) for national air quality monitoring programs. Since attempts to collect enough contemporary urban dust for this SRM had been faced with setbacks, production proceeded with the resuspension of the existing SRM 1649a Urban Dust to avoid further delays. Although SRM 1649a urban dust was collected in Washington, D.C. during the 1970's it remains a valuable material for intercomparison of methods and laboratories. The advantages of this feedstock are its immediate availability, its proven stability over time, and its known carbon composition. SRM 2784, a fine fraction of SRM 1649a, is expected to have a chemical composition that is similar to the raw material. Through future interlaboratory comparisons of bulk carbon, trace-carbon chemical speciation and carbon-isotope abundances, values will be assigned with the intention of certification.

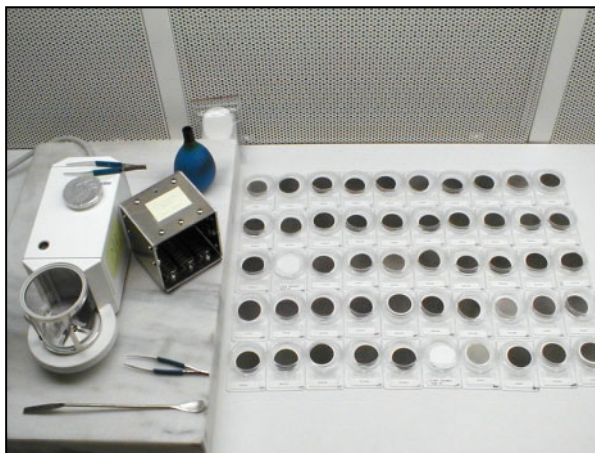


Figure 1. Filters loaded with fine urban dust (PM_{2.5}) are individually weighed (50 shown out of 2240). Filter-to-filter loading is visually variable, yet the mass distribution across any filter is within desired tolerances.

Purpose: Through the *Standard Materials for the PM 2.5 National Research Program*, interagency agreement DW13939042-01-0 between NIST and the US EPA, SRM 2784 has been designed and produced especially for the seven EPA “Supersites” that are monitoring fine airborne particulate matter (PM) throughout the U.S. SRM 2784 will provide the means to intercompare methods and laboratories for the measurement of black (elemental) carbon in PM. Use of this SRM will determine the level of agreement between sites and establish traceability to NIST for elemental and organic carbon measurements based on thermal-optical techniques.

Major Accomplishments: In collaboration with DRI and SRI, this year we have tared over 2000 filters, mounted these in especially designed holders, loaded these filters with the fine fraction of SRM 1649a through a PM resuspension/size segregation/filtration system, and determined the mass loading on each filter. We have also been able to evaluate this dust generation and collection system for producing up to 320 filters per run, allowing us to establish a method of delivering other dust materials to filters in

significant number and in a timely way to benefit other scientific communities faced with issues related to fine aerosol.

Impact: The basis for effective decisions lies in the accuracy and uncertainty of measurements, and the use of SRMs strengthens those measurements used as the first link in the long chain of environmental action. In a recent round-robin intercomparison involving both the atmospheric and ocean-sciences communities, black carbon measurements varied by more than a factor of six [Currie et al., submitted to Environmental Science and Technology, 2001]. Considering the importance of black carbon measurements related to climate forcing and human respiratory/pulmonary health, SRM 2784 is expected to play an indispensable role in PM measurement quality assurance, detecting biases across methods, laboratories, and applications, and improving PM metrology.

Future Plans: Next year, SRM 2784 will be made available after we characterize the filters for elemental carbon based on thermal-optical methods, and organize an intercomparison to assess the measurement reproducibilities within and across other methods. We shall also certify this material for total carbon, and provide speciated value assignments for carbon isotopes. The technology for producing aerosol filter SRMs will be commercially developed for other areas of research, *e.g.*, possibly bioaerosols, diesel soot and cigarette smoke for the health-sciences community.

Accuracy in Determining Atmospheric Elemental Carbon: Understanding the Response Surface of the Thermal-Optical Method

CSTL Program: Environmental Measurements

Authors: *J. Conny, and D. Klinedinst*

Abstract: Atmospheric elemental carbon (EC), i.e., black carbon, is a major pollutant from combustion sources that is responsible for as many as 50,000 premature deaths yearly in the U.S. Unfortunately, the definition for EC is very broad: it is chemically inert, refractory, and has extended aromatic rings. This leads to the pressing problem of how to measure it accurately. A set of methods now widely used by the EPA and the IMPROVE air visibility network for atmospheric aerosols is thermal-optical analysis (TOA). This method relies on a program for thermally desorbing particulate carbon on a filter in 7-8

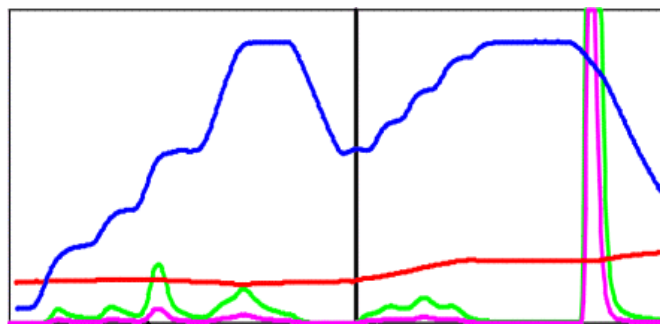


Figure 1. Time evolution of thermal-optical behavior for fine urban dust collected in Baltimore. Blue curve: temperature; green curve: hi-res FID response; magenta curve: lo-res FID response; red curve: reflectance of laser emission off dust; black vertical line: cut point between total organic carbon (left of line) and total elemental carbon (right of line). The spike in FID response on far right is from introduction of calibration gas.

steps while the filter is monitored for charring by laser transmittance or reflectance. Differences in EC/total carbon ratios between the TOA methods for the same sample depend largely on the temperature and duration of the temperature program steps. To quantitatively characterize how the TOA response depends on the factors in the temperature program for different types of aerosol samples, we have designed a study that maps the response surface using a fractional-factorial central-composite design.

Purpose: Soot pollution from combustion sources that include industry, transportation, forest fires, and domestic wood burning is a public health concern that causes up to 50,000 premature deaths yearly in the U.S. The major component of soot that impacts health is elemental carbon (EC). Accuracy in EC determination is problematic because wide-ranging values for the same atmospheric material are produced by different analytical methods, or by different operating conditions for the same type of method. This work is a response-surface study for understanding how thermal-optical analysis (TOA), a set of EC methods that are currently used extensively in the U.S., responds to changes in instrument operating conditions.

Major Accomplishments: TOA relies on a protocol for thermally desorbing carbon from particulate material collected on a filter. Desorption in either an inert (He) or oxidizing (He-O₂) atmosphere occurs in 7-8 temperature steps while charring on the filter is monitored by laser transmittance or reflectance. EC values from TOA depend largely on the temperature and duration of the thermal program steps. Measurements on three

sample types (forest fire emissions, urban dust (SRM 1649a), and indoor air) revealed widely-differing EC/total carbon ratios for two of the three sample types, depending on whether we used the temperature program employed by the EPA or the program employed by the Interagency Monitoring of Protected Visual Environments (IMPROVE) Air Visibility Network. A response surface study was designed for quantitatively mapping the TOA response surface using a replicated fractional-factorial central-composite design. The design consists of four factors: 1) maximum temperature in the He phase; 2) duration of the maximum He-phase temperature; 3) temperature and duration of the remaining He-phase steps; 4) duration of the 1st temperature step in He-O₂ phase.

Impact: A quantitative map of the TOA response surface will help scientists to derive the most appropriate instrumental conditions for accurately measuring EC by TOA. Due to the importance of TOA for assessing public health risk from atmospheric EC exposure, accuracy in EC by TOA may then help scientists find consensus on a more robust definition of EC.

Future Plans: This study will continue into FY02. 150 TOA measurements will be made on the three sample types to provide for replication in the study. New sample types will be considered for replicated measurements as we observe differences in the TOA response surface.

A Decade of Proficiency Testing of Laboratories involved in the Analysis of Airborne Asbestos

CSTL Program: Environmental Measurements

Authors: *S. Turner, E. Windsor, and E. Steel; O. Crankshaw (Research Triangle Institute); S. Leigh, and A. Rukhin (898)*

Abstract: In 1986, Congress mandated that NIST shall accredit laboratories involved in the analysis of asbestos in the nation's schools. The National Voluntary Accreditation Program (NVLAP) has administered the accreditation program for over a decade. The testing is conducted by a contractor - Research Triangle Institute (RTI) - with technical direction, oversight and support provided by CSTL. Proficiency tests have been sent twice yearly to between 65 and 125 laboratories per round since 1990. The testing program both flags laboratories with significant analysis problems and helps improve the analytical knowledge and capability of the laboratories in the program.

CSTL provides technical oversight and support to the program in several areas, including design of the proficiency test. The tests consist of a combination of paper tests, unknown materials on grids, and/or asbestos deposited onto filters or grids. CSTL also analyzes the test results. Significant effort has gone into evaluating the applicability of various statistical tests for analyzing asbestos deposited onto filters. At present, Grubb's test is used to determine outliers within a round of testing. Other tests (sum of logs test and binomial test) are used to determine outliers over the past six rounds of testing. Testing over many rounds enables the flagging of laboratories that have a bias towards counting high or low. Typically, 5-10% of the laboratories are flagged per round for counting bias and other errors.

Purpose: The major purpose of the proficiency testing program is to evaluate the capabilities of laboratories involved in the analysis of asbestos deposited onto filters (a separate program evaluates the proficiency of laboratories in bulk asbestos analysis). Those laboratories deemed deficient in their analyses do not retain their NVLAP accreditation unless corrective action is taken.

Major Accomplishments: Proficiency tests have been sent twice yearly to between 65 and 125 laboratories per round since 1990. CSTL has worked with a contractor, Research Triangle Institute (RTI), in the conduct of the tests. During this time, laboratories have been tested by a variety of means. Paper tests have been used to characterize the laboratories' ability to derive parameters related to the chemistry and structure of asbestos. Asbestos and nonasbestos samples deposited on grids have been used to test the laboratories' ability to identify phases. The laboratories have received filters containing asbestos to test their ability to adequately prepare and analyze samples. The laboratory analyses have been checked by both reanalysis by CSTL and RTI and by statistical analysis of the reported concentration values.

Impact: A major result of the proficiency testing is that laboratories having significant technical difficulties have been flagged. These laboratories are required by NVLAP to

correct their problems and, in some cases, are evaluated in a special onsite visit by a NVLAP assessor in order to be reaccredited. Another impact is the improved analytical knowledge level and capability of all the labs in the program. The proficiency testing program has provided laboratories with educational samples that are an aid in various aspects of asbestos analysis. The testing program has prompted many laboratories to further the education of personnel in various aspects of electron microscopy and asbestos analysis. Finally, several unanticipated problem areas encountered by laboratories have been highlighted, further aiding the reliability of the accredited labs' asbestos analysis..

Future Plans: The proficiency testing of laboratories is an ongoing program. CSTL will continue to provide technical analysis and oversight and help the laboratories continue to improve their analytical capabilities.

Fine Particulate Matter Source Attribution for Southeast Texas Using $^{14}\text{C}/^{13}\text{C}$ Ratios

CSTL Program: Environmental

Authors: *G.A. Klouda; K. Lemire, and D. Allen (University of Texas, Austin); and C. Lewis (U.S. EPA)*

Abstract: Air quality in the Houston area during the summer ranks among the worst in the Nation and is projected to exceed the National Ambient Air Quality Standard (NAAQS) for fine particulate matter (PM 2.5) with aerodynamic diameter less than 2.5 micrometer. Carbonaceous material makes up a significant portion of this aerosol yet little is known of its composition and sources. Biogenic aerosols in the southeast Texas region are believed to originate from forest fires, slash and agricultural burning, and secondary organic aerosol (SOA), the latter formed by reaction of biogenic precursors. To provide a better understanding of the biogenic sources of aerosol carbon in the region, PM 2.5 was collected in August 2000 during the Texas 2000 Air Quality Study (TexAQS 2000). A subset of the total samples were selected for ^{14}C measurement by NIST with the expectation of establishing possible limits to the amount of (uncontrollable) SOA contributing to the total PM 2.5. Its quantification is important in the formulation of realistic overall control goals for summertime PM 2.5. Radiocarbon analyses indicate that a substantial fraction of the aerosol carbon at an urban/suburban site, 27% to 73%, and at a rural, forested site, 44% to 77% was modern carbon.

Purpose: Our objective was to provide a direct measure of biogenic source contributions in southeast Texas.

Major Accomplishments: Air quality in the Houston area during the summer ranks among the worst in the Nation and is projected to exceed the National Ambient Air Quality Standard (NAAQS) for fine particulate matter (PM-2.5) with aerodynamic diameter less than 2.5 micrometer. Carbonaceous material makes up a significant portion of this aerosol yet little is known of its composition and sources. Biogenic aerosols in the southeast Texas region are believed to originate from forest fires (timber industry), slash and agricultural burning, and secondary organic aerosol (SOA), the latter formed by reaction of biogenic precursors. To provide a better understanding of the biogenic sources of aerosol carbon in the region, PM 2.5 was collected in August 2000 in the Houston-Galveston area during the Texas 2000 Air Quality Study (TexAQS 2000). A subset of the total samples collected were selected for ^{14}C measurement from two sites, Aldine and Conroe, with the expectation of establishing possible limits to the amount of (uncontrollable) SOA contributing to the total PM 2.5. Its quantification is important in the formulation of realistic overall control goals for summertime PM-2.5. Radiocarbon analyses indicate that a substantial fraction of the aerosol carbon at a urban/suburban site, 27% to 73%, and at a rural, forested site, 44% to 77% was modern carbon.

The levels of biogenic carbon aerosol as measured by the ^{14}C method is further evidence that biogenic volatile organic compounds emissions [Weidinmyer et al., 2000],

precursors to secondary organic aerosol, and biomass burning [Dennis, 2000] may contribute to fine particulate matter concentrations in southeast Texas.

Impact: These results will be included in models for developing effective strategies to meet National Ambient Air Quality Standards.

Future Plans: Additional ^{14}C measurements of total carbon, extractable organic carbon and black (elemental) carbon PM-2.5 are planned to provide source information on these specific chemical fractions from the Houston-Galveston area.

Reference:

Wiedinmyer *et al.* (2000), *Atmos. Environ.* 34, 3419-3435.

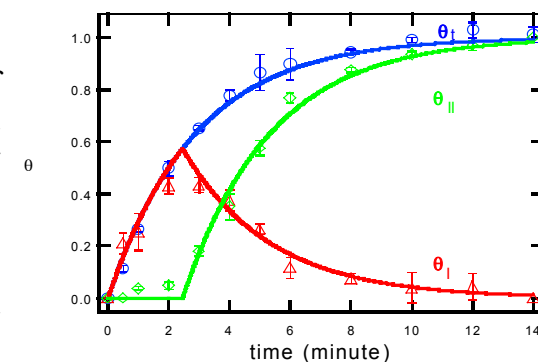
Dennis (2000), Inventory of air pollution emissions with forest, grassland and agricultural burning in Texas, M.S. Thesis, University of Texas, Austin, 2000.

An *In-situ*, Vibrationally-Resonant Sum Frequency Spectroscopy Study of the Self-Assembly of Dioctadecyl Disulfide on Au

CSTL Program: Chemical Characterization of Materials/Microelectronics

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

Abstract: The control of surface properties in solution deposited thin films underlies many technological applications. Optimization of the final film requires a fundamental understanding of the adsorption process on a molecular scale. *In-situ* spectroscopies, capable of real-time monitoring of surface processes, are essential to this understanding. Div. 837 in collaboration with Div. 844 are developing vibrationally resonant sum-frequency generation (VR-SFG) as an *in-situ* kinetic probe. This technique is demonstrated in a study of the assembly of perdeuterated dioctadecyl disulfide on Au substrates from ethanol solutions under laminar flow conditions. The coverage evolution of the VR-SFG spectra can be well described by the coexistence of two distinct phases: a low coverage, disordered phase and the full coverage crystalline phase. The structure of the adsorbed thiolate fragments is found to vary from a highly disordered state with significant gauche defects in the backbone, but a near normal orientation for the terminal methyl group at low coverages to the well characterized, upright, tilted, all-trans configuration characteristic of the crystalline full monolayer. The kinetics of the evolution of these two phases can be quantitatively described by a simple model evoking phase coexistence above a critical density of the disordered phase.



Total thiolate (blue), disordered phase (red), and crystalline phase (green) coverages vs time. Solid lines are fits to the two-phase model

Purpose: To demonstrate the applicability of VR-SFG, *in-situ* formation of self-assembled monolayers (SAMs) is studied. SAMs are ordered molecular assemblies formed spontaneously by the adsorption of a molecule with a certain affinity of its head group to the substrate. SAMs are excellent model systems for studies of monolayer structure, adhesion, and interfacial reactions, and have novel applications as biosensors, as nonlinear optical media, as corrosion inhibitors, and in molecular electronics. In order to understand the complex SAM formation dynamics, one must determine and understand the fundamental reaction steps of the self-assembly process. Second order nonlinear optical techniques such as VR-SFG are particularly suited for probing chemical reactions at buried interfaces due to their high surface selectivity, submonolayer sensitivity and excellent spatial, spectral, and temporal resolution.

Major Accomplishments: We conducted an *in-situ* SFG study of the assembly of SAMs from perdeuterated dioctadecyl disulfide on gold from ethanol solutions. *In-situ* spectra taken (Fig.1) under actual deposition conditions in real time combined with modeling

allow direct insight into the individual steps of the self-assembly. The SFG measurements allow independent determination of the total surface thiolate coverage and the internal molecular structure of the adsorbed thiolate. The uptake of surface thiolate was found to follow Langmuir kinetics, i.e. the probability of a molecule sticking to the surface is proportional to the available uncovered surface area.

The internal molecular structure of the surface species and their orientation is provided by detailed analysis of the vibrational spectra. CD_2 groups do not generate significant VR-SFG signal when the molecule is in an all-trans conformation. Therefore, the relative intensity of the CD_2 mode near 2100 cm^{-1} to the CD_3 modes near 2075 cm^{-1} (r^+) and 2220 cm^{-1} (r^-) is an indicator of internal structural order. Additional insight into the SAM structure can be obtained from consideration of the ratio of the intensities of the r^+ and r^- features. This intensity ratio can be related to the tilt angle of the methyl group from the surface normal.

The conformation and ordering of the alkane chain was found to be strongly dependant on coverage. Aspects of the low coverage structure including significant disorder in the methylene chain, but a near normal orientation of the terminal methyl, seem most consistent with an upright molecule with a disordered chain structure, consistent with the intermediate phase observed by STM for alkane thiol adsorption. In contrast, at high thiolate coverage, the methylene chains are highly ordered and the terminal methyl groups are well aligned with approximately 26° tilt angle. A simple model, in which the surface is covered with two molecular phases (disordered and crystalline) in dynamic coexistence, is found to well describe the evolution of molecular structure with surface density as shown in Fig. 2. The dynamic coexistence of the two phases naturally explains the observation of Langmuir kinetics.

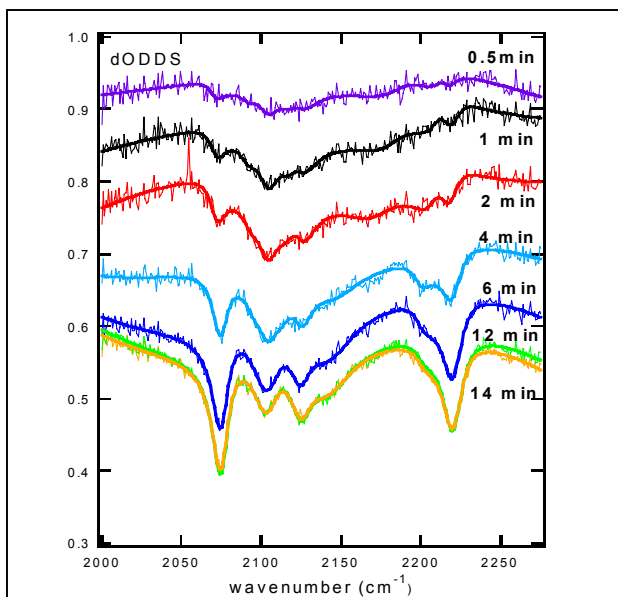


Figure 1: Selected VR-SFG recorded as a function of time following the introduction of dioctadecyl disulfide into the laminar flow cell. Each spectrum was recorded in 30 s.

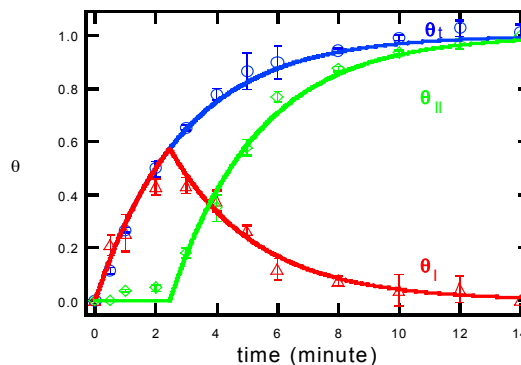


Figure 2: Total thiolate (blue), disordered phase (red), and crystalline phase (green) coverages vs time. Solid lines are fits to the two-phase model.

Impact: We have demonstrated VR-SFG as a powerful *in-situ* spectroscopic tool for the study of surface modification. The simple two-phase model naturally explains the ubiquitous observation of Langmuir kinetics and can lead to more realistic models for SAM formation.

Future plans: The use of surface-active agents to tailor the electrochemical deposition of copper is emerging as a critical technology for future semiconductor device fabrication, as it creates the superfill phenomenon essential for void free deposition in high aspect ratio vias. Although it is generally recognized that “copper inhibition” is critical to achieve superfill, the overall mechanism and the role of each additive in achieving superfill are still under debate. We will apply VR-SFG to the *in-situ* study of the adsorption of model additives used in Cu electroplating baths.