Applied Surface Science
Room 210A - Session AS-MoM

SIMS I - Cluster Probe Beams and General Topics

Moderator: I. Gilmore, National Physical Laboratory, UK

8:20am **AS-MoM1 Application of TOF-SIMS to Environmentally Relevant Surface and Interfaces*, D.J. Gaspar*,** *A. Laskin,* Pacific Northwest National Laboratory*; B.J. Finlayson-Pitts,* University of California, Irvine*; B.M. Sass,* Battelle Memorial Institute

TOF-SIMS analysis is an invaluable tool for analysis of environmentally relevant samples. The molecular identity and distribution of surface species can be essential in understanding environmental samples. In the Environmental and Molecular Sciences Laboratory, we have applied TOF-SIMS analysis to problems in atmospheric and environmental chemistry. Some examples presented here include: identification and measurement of fatty acids on aerosol particles, measurement of extent of reaction between NaCl and hydroxyl radicals,@footnote 1@@super ,@ @footnote 2@ investigation of the interaction between glass and gaseous nitric acid,@footnote 3@ and determination of heavy metal distributions in weathered, pressure-treated wood. In the first example, fatty acids were identified on field collected atmospheric aerosols as a function of time. Next, hydroxyl radicals were found to reacted with NaCl particles in the laboratory to produce basic species, while in the third example, the reaction products of gaseous nitric acid and borosilicate glass were determined to segregate on the glass surface in precipitates according to solubility. Finally, the distribution of copper, chromium and arsenic, as well as other metals, were measured in pressure treated wood after extended weathering. Each of these examples demonstrates the utility of TOF-SIMS in identifying species and determining distributions on environmentally relevant surfaces. @FootnoteText@ @footnote 1@ D.J. Gaspar, A. Laskin, W. Wang, S.W. Hunt, and B.J. Finlayson-Pitts. Applied Surface Science, in press, 2004.@footnote 2@ A. Laskin, D.J. Gaspar, W.H. Wang, S.W. Hunt, J.P. Cowin, S.D. Colson, B.J. Finlayson-Pitts. Science, 301 (2003) 340-344,"@footnote 3@ Y. Dubowski, A. L. Sumner, E. J. Menke, D. J. Gaspar, J. T. Newberg, R. C. Hoffman, R. M. Penner, J. C. Hemminger and B. J. Finlayson-Pitts. Physical Chemistry Chemical Physics, in press, 2004.

8:40am **AS-MoM2 Cluster Primary Ion Beam Secondary Ion Mass Spectrometry for 2 and 3 Dimensional SIMS Analysis*, G. Gillen*,** *P. Chi, A.J. Fahey, C.M. Mahoney, M.S. Wagner,* National Institute of Standards and Technology **INVITED**

The use of novel monoatomic and cluster primary ion beams for Secondary Ion Mass Spectrometry (SIMS) has several potential advantages for surface analysis. Cluster ion sputtering results in a reduced penetration depth for the constituent atoms of the cluster, which should improve SIMS depth resolution and minimizes the sputter depth over which the build up of the primary beam gives non-linear sputter and ion yield enhancements (the so-called transient region). Cluster bombardment may also reduce sputter-induced topography created during ion beam analysis of metal films. For organic surface characterization, cluster primary ion beam offers large improvements in sensitivity and, in selected cases, immunity to primary-beam-induced degradation of the sample. At NIST we are working on the application of novel primary ion beam SIMS for practical surface analysis. Several types of prototype ion sources are currently being evaluated for this application including; SF5+ , C8- and C60+. A variety of materials have been analyzed using these new ion sources including low energy ion implants of arsenic and phosphorous in silicon, boron delta-doped layers, surface metals, metal films, organic films and polymers. Recent key findings include the observation of improved depth resolution for semiconductor analysis and a reduction in beam-induced topography for metal films. Our most recent efforts have been focused on extending the cluster SIMS technique for the molecular depth profiling of organic thin films. Combined with secondary ion imaging we will demonstrate the unique capability of cluster SIMS to provide true 3 dimensional molecular surface analysis.

9:20am **AS-MoM4 Fundamentals and Applications of a New Bi-cluster Liquid Metal Ion Source*, F. Kollmer*,** *P. Hoerster, R. Moellers, D. Rading, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

In recent years Au cluster primary ions emitted from a LMIS (liquid metal ion source) have been successfully applied for the analysis of organic surfaces by TOF-SIMS. Compared to monoatomic primary ion bombardment the use of Au clusters leads to a considerable enhancement of the secondary ion yield up to several orders of magnitude. As the corresponding increase in the damage cross section is much smaller, the ion formation efficiency as a cumulative measure of the sensitivity of the analysis process, also increases significantly. In particular the Au cluster source combines the fundamental benefits of cluster ion bombardment with a high brightness source allowing to push the lateral resolution in organic imaging down to the 100-nm range. In this contribution fundamental as well as practical aspects of a newly developed Bi-cluster liquid metal ion source are addressed and compared with the capabilities of a Au cluster source. The Bi-cluster source offers excellent prospects for organic surface analysis since a large fraction of the primary ion current is emitted as singly and doubly charged clusters (up to Bi@sub 7@@super 2+@). Even at low emission currents stable operation is achieved which is advantageous with respect to the lifetime of the source and the spot size of the primary ion beam.

9:40am **AS-MoM5 TOF-SIMS Studies using a Newly Developed C@sub 60@@super +@ Primary Ion Gun: Fundamental Aspects and Applications*, R. Moellers*,** *F. Kollmer, D. Rading, T. Grehl, E. Niehuis,* ION-TOF GmbH, Germany

Recently it was shown that cluster primary ion bombardment leads to a considerable enhancement of the secondary ion emission efficiency for organic materials. This enhancement not only increases the sensitivity for molecular species up to several orders of magnitude, but also pushes the useful lateral resolution in organic imaging down to the sub-µm range. C@sub 60@ is currently discussed to be the most efficient projectile for organic surface analysis and first results have been published announcing depth profiling capabilities of C@sub 60@@super +@ primary ions on organic materials. We have integrated a newly developed C@sub 60@ ion gun into the TOF.SIMS 5. The gun can be operated both as sputter gun and as analysis gun with a primary ion energy of up to 20 keV using doubly charged C@sub 60@ particles. The new setup allows the direct comparison between different primary ions such as C@sub 60@@super +@, Au@sub 1@@super +@, Au@sub 3@@super +@ as well as the combination of metal cluster ions and C@sub 60@ in dual beam depth profiling. C@sub 60@@super +@ primary ions were used to extend our systematic investigation on the influence of different primary ion species, including metal cluster ions as well as monoatomic primary ions, on secondary ion parameters such as yield Y, damage cross section @sigma@ and efficiency E = Y/@sigma@. Those parameters have been evaluated for a variety of different sample materials and sample preparations allowing a classification of the merits of C@sub 60@ in different fields of application. Beside these fundamental aspects of cluster ion beam bombardment, the use of C@sub 60@@super +@ beyond the static limit on different samples will be highlighted.

10:00am **AS-MoM6 ToF-SIMS Quantitation of PDMS at the Surface of a Dehydrated Commercial Hydrogel Material*, J.A. Gardella, Jr.,*** State University of New York at Buffalo

The method of standard additions was performed in order to determine the amount of PDMS present at the surface of a dehydrated hydrogel material. Known amounts of a PDMS monomer were added to the surface and allowed to equilibrate. Peak ratios of 73Da (C3H9Si+):69Da(C4H5O+) and 147Da(C5H15Si2O+):113Da(C6H9O2+) were plotted against ng of PDMS added to the surface. A linear fit was applied to the data and the amount of PDMS present at the native surface was determined.

10:20am **AS-MoM7 SIMS Trace Uranium Measurements in HfO Films with the ims-1270*, A.J. Fahey*,** National Institute of Standards and Technology

The presence of radioactive elements, such as U, even at trace levels can make it impractical or impossible to use some materials in semiconductor applications because of randomly induced logic-errors from the decay of the radioactive element. Efforts have been put forth to determine the trace concentration of uranium in a HfO film deposited on Si. This measurement is complicated by the fact that high mass resolution is needed to resolve @super 178@HfSiO@sub 2@ from @super 238@U. In addition, high sensitivity is required in order to measure trace quantities of uranium in the film. The ims-1270 at the National Institute of Standards and Technology has been used for this purpose. Large magnetic sector SIMS instruments are not generally used by the semiconductor SIMS community because of their size and cost. However, they can address some very specific problems that cannot be addressed by smaller instruments that do not have the mass resolution or the transmission. A mass resolution of ~5000 is easily achieved with the ims-1270, while maintaining nearly full transmission. This condition can be used to separate the interference at U. An apparent concentration of U between ~1-10 ppm was measured is the available films. The measurement method, the data and attempted quantification of the measured concentration will be discussed.

10:40am **AS-MoM8 Improved Analysis of Bulk Insulators using Magnetic Sector SIMS with O@sub 2@@super +@ Primary Beam and Electron Beam Adjacent to Analysis Area***, F.A. Stevie, C. Gu, A. Pivovarov, R. Garcia, D.P. Griffis,* North Carolina State University

The application of a new method(1) for magnetic sector SIMS analysis of thick film and bulk insulators using O@sub 2@@super +@ primary beam with electron beam adjacent to the area of interest has been extended. Excellent results have been obtained for a wide range of bulk insulators, including SiO@sub2@, LiNbO@sub 3@, Al@sub 2@O@sub3@, AlN, and a low-K dielectric. Quantification of impurities in bulk insulators has also been demonstrated as evidenced by depth profiles of B implanted in silica, Ti in LiNbO@sub 3@, and Be in Al@sub 2@O@sub 3@. The 1E15 atoms/cm@super 3@ detection limit obtained for the Be in Al@sub 2@O@sub 3@ cannot be achieved using quadrupole analyzers because of the inability to filter the Al@super 3+@ mass interference. Profiles several micrometers deep have been routinely achieved. Accurate concentrations for several elements have also been obtained on NIST standard glasses. The analysis of the low-k dielectric was significant because direct electron bombardment results in decomposition of this material. While the efficacy of this method is indisputable, the apparently self compensating mechanism is not understood. It is clear that a conductive coating encompassing the sputtered area is required and that the electron beam must impact within approximately 100@micron@m of the analyzed area. While it is not clear which if any of these charge compensation mechanisms predominate, the most probable mechanisms contributing to positive charge compensation include secondary and/or backscattered electrons and electron beam induced conductivity (EBIC). Efforts to understand the charge neutralization mechanism for this method continue. (1) A. L. Pivovarov, F. A. Stevie, D. P. Griffis, Appl. Surf. Sci. (2004) in press

11:00am **AS-MoM9 Ionization of Al Atoms Emitted from Al Metal***, X. Chen,* University of California, Riverside*; Z. Sroubek,* Czech Academy of Sciences, Czech Republic*; J. Yarmoff,* University of California, Riverside

Ion-surface charge exchange is a central process in many surface analysis techniques, such as ion scattering spectroscopy (ISS), secondary ion mass spectrometry (SIMS) and electron stimulated desorption (ESD). Recently, we achieved a better understanding of homogeneous charge exchange between metal ions and metal surfaces, which gives a general insight for all the above techniques and is especially critical in analysis of SIMS data. Atomically clean and modified Al (100) surfaces in ultra-high vacuum were bombarded by 2 and 5 keV Xe@super +@ ions. The absolute ionization probability of energetic (> 500 eV) recoiled particles was measured with time-of-flight, and then used to calibrate the energy and angular distributions of low energy (10-600 eV) sputtered ions collected with an electrostatic analyzer. The independent particle model of non-adiabatic surface-atom charge-exchange, which has typically been used to analyze single scattering events, is shown to accurately describe all of the experimental data from a few eV (typical sputtering energy) to the keV (typical scattering and recoiling energy) range. Extensions of this work to other clean metal surfaces, such as Fe, which has a d-band, will be discussed. Also, we plan to perform homogeneous scattering experiments with a novel liquid metal ion source (LMIS), to determine absolute homogeneous ionization probabilities for well-defined trajectories.

Applied Surface Science
Room 210A - Session AS-MoA

SIMS II - Biological and Organic

Moderator: G. Gillen, National Institute of Standards and Technology

2:00pm **AS-MoA1 Single Photon Ionization of a Derivatized Peptide Covalently Bound to a Surface***, P.D. Edirisinghe, S.S. Lateef, C.A. Crot,* ***L. Hanley****,* University of Illinois at Chicago*; J.F. Moore, W.F. Calaway, M.J. Pellin,* Argonne National Laboratory

Covalently bound peptides, proteins, and other biomolecules are widely used for microarrays, microfluidic channels, cell growth surfaces, and biosensors. Detection of these surface bound species by matrix assisted laser desorption ionization or secondary ion mass spectrometry (SIMS) is often complicated by low ionization yields and/or high fragmentation. Single photon ionization is one method that shows great promise for enhancing ionization yields with a minimum of fragmentation. The fluorine excimer laser is an intense laboratory source of vacuum ultraviolet radiation, but the 7.87 eV photons it generates are lower in energy than the ionization potential of many target species. A method is described here whereby derivatization of peptides with the Fmoc group allows efficient fluorine laser single photon ionization of the entire labeled peptide. Various Fmoc labeled peptides are covalently bound to oxidized Si(100) wafers via maleimide coupling to surface bound aminopropyltriethoxysilane. Physisorbed films of Fmoc labeled peptides, unlabelled peptides, and various amino acids are prepared by drying a solution thereof onto the silicon wafer. Both covalently bound and physisorbed peptides are analyzed by laser desorption photoionization (LDPI) mass spectrometry. Only the Fmoc labelled peptides form large ions identified as common peptide fragments bound to either Fmoc or the surface linker. Unlabelled peptides and amino acids do not form large representative ions. Electronic structure calculations performed with Gaussian 98 indicate the Fmoc label is behaving as an ionization tag for the entire peptide, lowering the ionization potential of the complex below the 7.87 eV photon energy. This method should allow detection of many molecular species covalently or electrostatically bound to surfaces.

2:20pm **AS-MoA2 ToF-SIMS Applications in the Analysis of DNA Microarrays***,* ***K.K. Soni****,* Corning Incorporated

DNA arrays are typically prepared by microcontact printing of DNA on a glass surface that has been modified by an aminosilane. The DNA immobilization on the modified glass surface relies on direct contact between DNA and amine groups supplied by the silane layer. The presence of surfactants such as Triton even at trace level can completely inhibit attachment of DNA. Given the tendency of this molecule to segregate at interfaces, its detection by surface sensitive techniques such as ToF-SIMS is facilitated; in other words, the sample preparation method and ToF-SIMS analysis constitute a very sensitive analytical procedure to detect trace levels of surfactant molecules in DNA preparations. To further corroborate the impact of surfactants, pure DNA solutions were intentionally contaminated with Triton X-100 in varying concentrations. The resulting mixtures were used for printing on modified glass slides. It was demonstrated that the presence of Triton reduces the amount of immobilized DNA and above a certain concentration (10-100 ppm by volume) can completely inhibit DNA printing. In another application of ToF-SIMS, we demonstrate the ability to study fluid flow and evaporation dynamics in a drying droplet in microarrays. Evaporation behavior of the drop strongly influences the solute transport and hence the uniformity of the dot. We have utilized ToF-SIMS analysis of printed DNA dots to determined the final distribution of the solute by mapping the sodium concentration in the drop. Three different kinds of effects were observed: the first kind having higher concentration of solute on the outer edge of the drop (rim effect); the second kind having higher concentration at the center of the drop (pinprick) and the third having uniform distribution.

2:40pm **AS-MoA3 Cell Imaging, DNA Diagnostics, Protein Analysis: Mass Spectrometric Characterization of Biological Surfaces***,* ***H.F. Arlinghaus****,* Physikalisches Institut der Universität Münster, Germany **INVITED**

We have used time-of-flight secondary ion mass spectrometry (TOF-SIMS) and laser postionization secondary neutral mass spectrometry (Laser-SNMS) to analyze various biological surfaces. Both techniques use a focused energetic primary ion beam for bombarding a solid sample, and a mass spectrometer for analysis. But unlike SIMS, which analyzes only the sputtered secondary ions, Laser-SNMS uses laser beams to either resonantly or non-resonantly ionize the majority of sputtered neutral particles. In our presentation, we will compare and discuss the salient characteristics of the TOF-SIMS and Laser-SNMS techniques and will show applications in the following fields: (a) imaging and quantifying target-specific drug delivery systems as well as intrinsic elements and molecules in single cells with subcellular resolution in vitro, i.e. in cell cultures, and in vivo, i.e. in tissues, (b) investigation of the immobilization process of PNA and the influence of length and type of spacer molecules on the efficiency of hybridizing DNA to PNA biosensor chips and investigation of its use for DNA diagnostics with unlabeled DNA, (c) detection of proteins in cells, and (d) investigation of yield behavior and fragmentation patterns using different primary ions (Ar@super +@, Xe@super +@, SF@sub 5@@super +@, Au@super +@, Au@sub n@@super +@) for increasing efficiency and sensitivity in cell and DNA diagnostics. Furthermore, we will discuss current instrumental developments, particularly in regard to 3D molecular imaging with nanometer-scale resolution. We will show that TOF-SIMS and Laser-SNMS are well suited for imaging and quantifying trace element and molecule concentrations in biological materials with very high efficiency and nanometer-scale resolution. In particular, TOF-SIMS has the potential for providing a new method for rapid unlabeled DNA diagnostics, and its high detection efficiency makes this technique especially useful for directly analyzing genomic DNA.

3:20pm **AS-MoA5 Molecular Depth Profiling of Polymer Multilayers using a Polyatomic Primary Ion Beam***,* ***M.S. Wagner****,* National Institute of Standards and Technology

Obtaining characteristic molecular information during the secondary ion mass spectrometry (SIMS) depth profiling of polymers has been severely limited due to primary ion-induced sample damage when using monatomic primary ions. Polyatomic primary ions have shown promise for the molecular depth profiling of thin (< 250 nm) polymer films due to their low penetration depth and high sputter rates. In this study, dual-beam time-of-flight SIMS (sputter ion = 5 keV SF@sub 5@@super +@, analysis ion = 10 keV Ar@super +@) was used to depth profile spin-cast multilayers of poly(methyl methacrylate), PMMA, poly(hydroxyethyl methacrylate), PHEMA, and trifluoroacetic anhydride-derivatized PHEMA, TFAA-PHEMA, on silicon substrates. Despite extended SF@sub 5@@super +@ bombardment (> 5 x 10@super 14@ ions/cm@super 2@), characteristic pendant-group-related positive and negative secondary ions of the different polymer layers were observed as a function of depth during the depth profiles. The sputter rates of the polymers in the multilayers typically were lower than corresponding single layer films, with the ion-induced damage accumulation rate of the outermost polymer layer affecting the sputter rate of the underlying layers. Due to its higher ion-induced damage accumulation rate, PHEMA lowered the sputter rates for underlying PMMA or TFAA-PHEMA layers. Similarly, PMMA reduced the sputter rate for underlying TFAA-PHEMA layers. Typical interface widths between adjacent polymer layers were 10-15 nm for the bilayer polymer films; however, the layer order significantly impacted the interface widths for trilayer films. The interface widths in the trilayer films increased with depth to ~ 35 nm, showing the formation of sputter-induced surface roughness during depth profiling of these films. This study demonstrates the utility of polyatomic primary ions for molecular depth profiling and presents new opportunities for the characterization of thin polymer films.

3:40pm **AS-MoA6 Applications of Cluster SIMS for Molecular Depth Profiling in Biomaterial Systems***,* ***C.M. Mahoney****,* National Institute of Standards and Technology*; J.-X. Yu, J.A. Gardella, Jr.,* State University of New York at Buffalo*; A.M. Johnson, R. Langer,* Massachusetts Institute of Technology

Polymeric biomaterials have numerous clinical applications including as surgical implants, absorbable sutures, tissue engineering scaffolds and drug delivery devices. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has proven to be particularly useful in the surface analysis of these polymeric biomaterials@super 1@. However, much of this work has been done with monoatomic primary ion beams, which have a large amount of beam-induced damage associated with them. This precludes the ability to obtain in-depth information from organic samples. Compared to monoatomic ion bombardment, cluster primary ion beams, such as SF@sub 5@@super +@ have resulted in decreased subsurface damage and increased sputter rates in some cases, allowing the ability to depth profile in organic and polymeric materials for the first time@super 2-3@. This talk will briefly describe the ongoing research efforts at NIST to further develop cluster SIMS as a tool for biomaterials characterization. We have already shown the ability to depth profile in model polylactic acid (PLA) based drug delivery systems using cluster SIMS@super 3@. More recently, we have been able to successfully measure the extent of preferential segregation in polylactic acid / polyethylene glycol (PLA/PEG) blends as well as determine the in-depth distribution of acetamidophenol doped PLA films as a function of increasing degradation time. We have also successfully obtained information as a function of depth in a novel drug delivery microchip. This work further demonstrates the increasing utility of cluster SIMS for biomaterials applications. @FootnoteText@ @footnote 1@ Lee, J.-W.; Gardella, J.A. Jr. Analytical Chemistry 75 (2003) 2950-2958.@footnote 2@ Gillen, G.; Roberson, S.; Rapid Commun. Mass Spectrom. 12 (1998) 1303.@footnote 3@ Mahoney, C.M.; Roberson, S.V.; Gillen, J.G. in "Depth Profiling of 4-Acetamidophenol Doped Poly(lactic Acid) Films Using Cluster SIMS"; Analytical Chemistry, Accepted March 2004.

4:00pm **AS-MoA7 Improved ToF-SIMS Ion Yields and Cationization of Water-Soluble Analytes by Polyelectrolyte Multilayers***, **Y.-Y. Lua**, C.A. Pew,* Brigham Young University*; A. Schnieders,* ION-TOF USA, Inc.*; P.B. Savage, R.C. Davis, M.R. Linford,* Brigham Young University

Arguably one of the most important issues that has faced time-of-flight secondary ion mass spectrometry (ToF-SIMS) since its inception more than 30 years ago is the need for improved ion yields from analytes. Here we describe an entirely new method for improving ion yields and cationizing analytes that is particularly effective for charged, water-soluble species. This approach takes advantage of the highly charged, ionic nature of polyelectrolytes and the ease with which they can be deposited onto surfaces by the well known layer-by-layer method. In particular, we show that after an ultrathin film (ca. 0.5 nm) of a polycation (polydiallyldimethylammonium chloride, PDADMAC) spontaneously adsorbs onto a silicon (oxide) surface, a mixture of a polyanion (poly(sodium 4-styrenesulfonate)) and a water-soluble analyte, which contains one or more basic nitrogen atoms, will adsorb to form a second layer (ca. 1.5 nm thick). ToF-SIMS of this bilayer shows a significant enhancement in quasi-molecular analyte ion yield (roughly a ten-fold increase in signal), compared to that of the pure compound, or the compound dissolved in dilute HCl and dried on a surface. This phenomenon is demonstrated for two large organic macrocycles (m/z 672 and 745), and a smaller aromatic compound (acridine, m/z 179). Similarly, a significant enhancement in the ion yield of the quasi-molecular ion of 9-anthracenecarboxylic acid (m/z 222) is observed when it spontaneously deposits with PDADMAC to form a ca. 0.5 nm film on silicon.

4:20pm **AS-MoA8 Three-Dimensional Reconstruction of Elemental Distributions from TOF-SIMS Image Depth Profiles***, **S.R. Bryan**, D.G. Watson,* Physical Electronics USA

Time-of-flight Secondary Ion Mass Spectrometery (TOF-SIMS) is a powerful techique for image the distribution of elements and organic molecules on surfaces with with spatial resolution down to 100 nm. When combined with sputter depth profiling, TOF-SIMS can characterize the 3-dimensional distribution of all elements in the near surface region of materials. Due to the parallel detection nature of the TOF-SIMS technique, the full 3-dimentional data can be acquired for all elements in a reasonable amount of time. The challenge is to effectively display the tremendous amount of information generated in an image depth profile. The use of one or two cross-section images does not adequetly display the 3-dimensional distributions. In this work, we have applied methods developed in the medical field for CT and MRI imaging to TOF-SIMS data. Through the use of isosurface reconstruction and translucent display, the full 3-dimensional distribution of multiple elements can be viewed simultaneously.

Applied Surface Science
Room Exhibit Hall B - Session AS-MoP
Poster Session

AS-MoP1 Producing Substrates for MALDI-MS by Chemomechanically Scribing Silicon and Glass.*, R. Blake*, *G. Jiang, C. Thulin, M.R. Linford,* Brigham Young University

Miniaturized matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) sample supports have been developed on silicon and glass for improving analysis sensitivity and reproducibility of biomolecules. Clean silicon and glass were silanized with a fluorinated compound that produces extremely hydrophobic surfaces. After silanization 200 micron diameter hydrophilic anchors were chemomechanically scribed with a diamond tip onto silicon and glass in the presence of water. These hydrophilic areas pin aqueous solutions of matrix and peptide. As the water evaporates the matrix and peptide are pinned to the hydrophilic areas, concentrating and localizing the analyte to a small spot that is fully covered by the ionizing laser beam. Thus, both sensitivity and reproducibility of the analysis are simultaneously improved. MALDI-MS spectra of water soluble peptides, glufibrinopeptide B and angiotensin II, with 2,5-dihydroxy benzoic acid (DHB) as matrix on silicon or glass substrates showed the expected improvements both in sensitivity and reproducibility. Compared to previous reports, this method of making miniaturized MALDI-MS sample supports is rapid, cheap, and could be undertaken in a typical laboratory.

AS-MoP2 TOF-SIMS Investigation of Selected Excipients in Color Coated Placebo Tablets*, X. Dong*, *C.A.J. Kemp,* Eli Lilly and Company

Time of Flight-Secondary Ion Mass Spectrometry (TOF-SIMS) was applied to investigate the surface and cross-section of placebo tablets. Eight excipients, including lactose, hydroxypropyl cellulose (HPC), and microcrystalline cellulose (MCC) were examined, as well as color coat mixture and polishing material used in placebo tablets. The investigation of raw materials shows that HPC can be distinguished from other excipients based on its unique peaks present in positive ion TOF-SIMS spectra. Most peaks observed in the spectra of MCC were also detected in the spectra of lactose, which makes it difficult to distinguish MCC from lactose. The comparison between the spectra obtained from tablet surface and cross-section shows that the chemical composition of tablet surface is different from that of bulk. Mg, which comes from a polishing material used on the outside of the tablet, dominates placebo surface spectra, while Na, which is one of constitutes of several excipients, dominates the cross-section spectra. In addition, peaks corresponding to HPC were much more abundant in the surface spectra than in the cross-section spectra, comparing to peaks corresponding to MCC/lactose. The preliminary results suggest that HPC might migrate more easily to sample surface than MCC and lactose during the tablet manufacturing process. The possibility of surface contamination is relatively low, since HPC related peaks were consistently found in surface spectra of all placebo tablets examined, as well as one house drug tablet analyzed in previous work.

AS-MoP3 Cluster Primary Ion Bombardment Facilitates ToF-SIMS Analysis of Biological/Tissue samples*, V.S. Smentkowski,* General Electric Global Research Center*; A. Schnieders,* Ion-Tof USA, Inc.*; F. Kollmer,* Ion-Tof GmbH*; R. Kersting,* Tascon GmbH, Germany*; J.A. Ohlhausen, M.R. Keenan, P.G. Kotula,* Sandia National Laboratories

Biological/tissue samples present a number of analytical challenges including the detection of trace quantities of high mass species within large (few mm) areas of samples. Recent advances in both ToF-SIMS instruments (such as stage rastering and liquid metal polyatomic ion sources) and data reduction protocol are facilitating biological/tissue analysis. In this poster, we will compare ToF-SIMS spectra and images collected using both Ga (mono-atomic) and Gold 3 (polyatomic) primary ion sources on treated brain tissue sections. Using polyatomic gold we are able to detect and image high mass (> 1,500 amu) species; these species were not detected in the spectra collected using Ga (even with a higher Ga primary ion fluence). The wealth of information contained in spectral images collected using polyatomic gold is tremendous, and the resulting spectral images can be difficult to interpret. In this poster we will also demonstrate that Multivariate Statistical Analysis (MVSA) tools such as AXSIA (Automated eXpert Spectrum Image Analysis) are useful for deconvoluting the spectral images. Using AXSIA, we are able to separate low yield species from high yield species in the high mass (ca. 760 amu) region of the ToF-SIMS spectra. The AXSIA component of this work was funded in part under CRADA SC00/01609 PTS 1609.02 (GE/Sandia). Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AS-MoP4 Using ToF-SIMS as a High Throughput Screening Tool for Lightweight Hydrogen Storage Materials*, J.P. Lemmon,* *J.-C. Zhao, V.S. Smentkowski,* General Electric Global Research Center

Combinatorial Chemistry (CC) coupled with High-Throughput Screening (HTS) techniques are being used at the General Electric Global Research Center to generate and characterize multi-component samples in order to accelerate the discovery of new hydrogen storage materials for automotive applications. In order to meet the DoE target of 6 weight percent hydrogen by the year 2010, the hydrogen storage material must contain low Z (low weight) components. Low Z elements can not be detected using techniques that rely on X-ray generation, such as Electron Probe Microanalysis (EPMA) and/or X-Ray Fluorescence (XRF). ToF-SIMS is ideally suited for the rapid screening of low Z materials since it allows for the detection of all elements and can also image large areas (eg. 70mm x 70mm) in less than 2 hours. ToF-SIMS images can be measured while the combinatorial chemistry library is being heated and/or maintained at the desired temperature in the range of 100 to 600° C. Temperature programmed ToF-SIMS experiments will be used to measure the hydrogen desorption processes of combinatorial chemistry libraries. Select examples will be presented.

AS-MoP5 Comparative Analysis of a Pt/Rh Catalyst Sample with TOF-SIMS and Laser-SNMS*, A. Schnieders,* ION-TOF USA, Inc.*; F. Kollmer,* ION-TOF GmbH, Germany*; M. Fartmann, H.F. Arlinghaus,* Universität Münster, Germany*; V.S. Smentkowski,* General Electric Global Research Center

In the field of catalysis, the analyst often needs to detect and image the distribution of trace quantities of species within the top most surface layer. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a well-established technique for such analysis. Unfortunately, quantitative TOF-SIMS analysis is not always easy to accomplish. Laser postionization of sputtered neutrals (Laser-SNMS) provides a higher sensitivity for many elements than TOF-SIMS, and in case of non-resonant multiphoton ionization (NRMPI), Laser-SNMS also provides for more uniform useful yields over the whole elemental range, thus enabling a more straight-forward way of quantification. In this paper, we compare the use of TOF-SIMS and Laser-SNMS with NRMPI for the analysis of a noble-metal treated stainless steal catalyst sample. The main analytical question focused on the determination of the lateral distribution of Pt and Rh on the surface of an actual (dirty) sample. Despite the relative low sensitivity for Pt, TOF-SIMS analysis enabled the determination of the lateral distribution of Pt and Rh on the surface. Quantification of these metals was possible by normalizing the corresponding ion intensities to those of a matrix signal. In comparison to TOF-SIMS, Laser-SNMS provided higher sensitivities for Pt and Rh as well as for other metals detected on the surface. To obtain accurate quantification, relative sensitivity factors for Pt and Rh were established on control samples. The lateral distributions thus measured confirmed those determined with TOF-SIMS. The similar results obtained with both techniques allowed establishing a procedure for quantification of TOF-SIMS results on similar samples.

AS-MoP6 Application of Time Interpolation to SIMS Isotopic Ratio Measurements*, D. Simons*, *K.J. Coakley, A.M. Leifer,* National Institute of Standards and Technology

Secondary ion mass spectrometry (SIMS) can be used to perform localized isotopic ratio measurements on a micrometer scale. Such measurements have broad applicability in areas of biology, geology and astronomy. A specific application area of recent interest is nuclear forensics, whereby SIMS has been applied to the search for evidence of uranium enrichment activities through the measurement of the relative abundances of U-235 and U-238 in micrometer-sized particles. In SIMS measurement systems, the count rate of isotopes may vary in time as a limited sample quantity is consumed during the analysis. Since only one isotope at a time is measured in conventional ion counting detection systems, this drift can introduce systematic error into the estimate of the ratio of any two isotopes. Hence, correcting the data for drift is critical to the accurate determination of isotopic ratios and their associated uncertainties. We consider isotopic measurements in a pairwise fashion, with the more abundant isotope of the pair designated as the major isotope and the less abundant one as the minor isotope. We correct the measurements for drift by aligning the major and minor time series of isotopic pairs by use of linear interpolation. We estimate an isotopic ratio for each of two cases. In one case the time series of the more abundant isotope is aligned with respect to the time series of the less abundant isotope. In the second case the less abundant isotope is aligned with respect to the more abundant one. We average both of these estimates to get a drift-corrected estimate. We present an analytical formula for the uncertainty of the isotopic ratio which accounts for correlation introduced by interpolation. We also present an approximate hypothesis test procedure to detect and quantify possible time-dependent drift of the measured isotopic ratio during a single analysis.

AS-MoP7 Carbon Mediation on the Growth of Self-Assembled Ge Quantum Dots on Si (100) by Ultra High Vacuum Chemical Vapor Deposition*, **P.S. Chen,*** Electronics Research & Service Organization, Industrial Technology Research Institute, Taiwan, Republic of China*; S.W. Lee,* Industrial Technology Research Institute, Taiwan*; M.-J. Tsai,* Electronics Research & Service Organization, Industrial Technology Research Institute, Taiwan*; C.W. Liu,* Industrial Technology Research Institute, Taiwan

The growth of self-assembled Ge quantum dots (QDs) with carbon mediation on Si (100) by a hot wall ultra-high-vacuum chemical vapor deposition system with different growth temperatures and surfactant gas flow rates was investigated. The ethylene (C@sub 2@H@sub 4@) and methylsilane (SiCH@sub 6@) gas were as surfactants prior to the growth of Ge QDs, respectively. Small dome-like Ge QDs were observed after carbon treatment as compared to the hut shaped Ge cluster without any carbon pre-treatment at 550 °C. Those dome-like Ge QDs have a mean base width and height of about 40 and 5 nm, respectively, and the density is about 6.7 ï,´ 10@super 9@ cm@super 2@ at the growth temperature of 550 °C. Comparison with boron mediation, strong Câ?"H bonds during the epitaxy growth play different roles and lead to this dramatic modification of Ge QDs morphologies. Furthermore, multifold Ge/Si layers were also carried out to enhance the emission intensity with first Ge layer treated by C@sub 2@H@sub 4@) and avoid the generation of threading dislocations.

AS-MoP8 Field Emission Analysis and Optimization of Carbon Nanoflake Edge Emitters*, **X. Zhao**, R.A. Outlaw, J.J. Wang, M.Y. Zhu, D.M. Manos, B.C. Holloway,* College of William and Mary

Ultra thin carbon nanoflake (CNF) films have been inductively grown by rf chemical vapor deposition on a variety of substrates. The CNF films grow vertically with respect to the substrate and have flake thicknesses of < 2 nm with terminating edges as small as a single atom layer (graphene). The inordinately high field enhancement factor of the flakes represents a high tunneling efficiency and electron emission. In addition, the packing density of the flakes is also extremely high suggesting that CNF films have great potential as field emission cathodes. To optimize the field emission from these films, the growth conditions, deposition temperature, deposition time and chemical composition were varied. The turn-on field, I-V behavior, noise level, robustness, maximum current density and field emission energy spectra for selected deposition condition were observed. The CNF films were also coated with thin layers of Ti, Zr and Hf and heated to form low work function carbide edges. The resulting characteristics were then compared to uncoated CNF. Adsorption effects of H@sub 2@O and H@sub 2@ for both the uncoated and coated CNF were also studied.

AS-MoP9 Ti Metal Cluster on the Carbon Nanotube*, **S. Lee**, H. Kim, J. Lee, B.Y. Choi, Y.S. Cho, Y. Kuk,* Seoul National University, South Korea

Junctions between metal and carbon nanotube (CNT) have been investigated mainly with transport experiments for the last several years. However, their detailed electronic and geometric structures are not fully revealed. We have created junctions between CNT and Ti metals by depositing the metal on CNT and the electronic and geometric structures have been studied with low temperature scanning tunneling microscopy. Ti metal is preferentially coated near the edges and in the gaps between CNTs. In spatially resolved tunneling spectroscopy, the metallic states are observed on Ti surfaces and the state extended into CNT area, suggesting the existence of mixed states near the junctions@footnote 1@. The origin of the mixed states and observed screening lengths will be discussed. @FootnoteText@ 1) S. Dag, E. Durgun, and S. Ciraci, Phys. Rev. B 69, 121407(R) (2004).

AS-MoP10 Depth Resolution of Inverse Calculation from ADXPS to Depth Profile*, **A. Tanaka,*** Physical Electronics, Japan*; D.G. Watson,* Physical Electronics USA

A practical inverse calculation method is discussed which transforms the data from angle dependent x-ray photoelectron spectra (ADXPS) to depth profile using a maximum entropy method. The depth resolution of the method is evaluated using an 84%-to-16% resolution, which is less than 0.7 nm for natural oxide when optimizing 5 take off angle data. Theoretical comparison is also discussed.

AS-MoP11 Study of the Oxidation Behavior of Aluminum and Aluminum Alloys Using X-Ray Photoelectron Spectroscopy*, G.D. Claycomb, **P.M.A. Sherwood**,* Kansas State University

The oxidation behavior of high purity aluminum and two aluminum alloys, after exposure to a variety of aqueous environments, has been studied by using core and valence band X-ray Photoelectron Spectroscopy. Freshly abraded samples were exposed to de-oxygenated, normal and oxygenated quadruply distilled water for one hour at room temperature, 40Âº, 70Âº and 100ÂºC. For pure aluminum, single oxidized aluminum compounds were formed in some instances while mixtures were formed in other cases. For the alloys, the oxidized aluminum compounds were mixed with oxides of the alloying elements in some instances and in other cases where the films had thickened sufficiently, single oxidized aluminum compounds were found on the outermost surface. Identification of the types of oxides being formed was achieved by using valence band photoelectron spectrum. The spectra were analyzed by using a comparison with the valence band spectra of known oxidized aluminum compounds and spectra generated by additions of the spectra from the known oxidized aluminum compounds together with approaches that used difference spectra. This work is based upon work supported by Luxfer Gas Cylinders.

AS-MoP12 Chemical State Analysis Boron and Phosphorus on Si Wafer Surface Measured by TRXPS*, **Y. Iijima**, T. Tazawa,* JEOL, Japan

It is well known that x-ray photoelectron spectroscopy (XPS) is a meaningful analytical technique for the chemical characterization of material surface, but the detection limit of XPS is inferior to that of other methods, such as secondary ion mass spectrometry (SIMS) and total reflection x-ray fluorescence (TXRF) analysis. Recently, in developing a new DRAM, the energy of P and B injected into an Si wafer was bound to be lowered. Accordingly, the investigation of the chemical bonding states of these elements on the Si wafer surface has become important. Since B1s and P2p photoelectron peaks overlap with the energy loss peaks of Si2s and Si2p peaks, it is difficult to detect a small amount of B and P injected into the Si wafer by XPS. Therefore, the use of x-ray total reflection has become noteworthy in photoelectron spectroscopy. This is because TRXPS (total reflection x-ray photoelectron spectroscopy) can greatly reduce the number of inelastically scattered electrons contributing to the background of photoelectron spectrum, as the effective analysis depth of TRXPS is nearly equal to the x-ray penetration length in the solid. In addition to this, TRXPS is expected to give a lower detection limit. In this work, we examined the chemical bonding state of B and P on the Si wafer by means of TRXPS. In what follows, the effectiveness TRXPS method to the semiconductor surface analysis will be described.

AS-MoP13 XPS Characterization of Ingaalp/ingap Quantum Well Structures*, **Y.J. Yoon**, L.V. Yashina, B.Y. Kim, V. Kureshov,* Samsung Electro-mechanics Co., Ltd, Korea

InGaAlP/InGaP heterostructures are important for light emission in laser diodes. Post growth characterization of InGaAlP solid solution composition is actual problem in the optimization of growth parameters due to compositional dependent mismatch and Eg value. The mismatch is mostly influenced by Ga/In ratio, whereas Eg is governed by Al/Ga ratio. In practice the set of accessible diagnostic procedures is limited by photoluminescence study and XRD. For the quasibinary solid solution composition can be estimated using lattice constant or Eg dependences on mole fraction whereas for the quaternary solid solution this approach can not be applied rigorously. The use of direct analytical techniques is complicated by many factors such as low thickness of layers, restrictions in depth resolution, surface preparation problem. InGaAlP/InGaP multilayered structures with layer thickness ~ 5 nm were studied by XPS. The superlattices were obtained by MOCVD on GaAs(100) substrate. XPS study was carried out using monochromatic Al Ka source in Quantera SXM. Two independent procedures were applied: (1) sputtering depth profiling and (2) Angle dependent photoemission registration for the samples containing well/barrier interface in the layer under analysis. In 3d, Ga 2p, Al 2s, P 2s peak intensities were calibrated using the set of reference alloy samples InGaP, InAlP and pure compounds InP, GaP. Sputtering rate compositional dependence was also taken into account. Sputtering was carried out using Zalar rotation to reach maximal depth resolution. For the depth profiles analysis attenuation length and surface roughness after sputtering, estimated by AFM, were taken into consideration. The obtained results are compared with SIMS data.

AS-MoP14 XPS, AFM, and Confocal Microscopy Data Correlation: Characterization of Polymer Blend Systems to Create a 3D Volume*, **J.L. Fenton**, K. Artyushkova, J. Farrar, J.E. Fulghum,* The University of New Mexico

No single non-destructive technique readily provides both surface chemistry and component distribution through the depth of polymer samples. Visualization based upon multiple analytical characterization techniques can be used to create a 3-D map of polymer chemistry. This work combine data from XPS, AFM, and confocal microscopy analysis of polyvinylchloride/polymethylmethacrylate and polystyrene/polybutadiene blends. Confocal microscopy images are used to create a volume that can be correlated with XPS images and spectra in order to semi-quantitatively map the distribution of chemical components within the blends. The correlated data will be combined with AFM images to incorporate surface topography measurements. This work has been partially supported by NSF CHE-0113724 and the NSF IGERT CORE program.

AS-MoP15 Auger Analysis of Corrosion Scale Formed on a Ni-Cr-Fe Alloy by Exposure to Supercritical Water at Elevated Temperature.*, **S.A. Wight**, J.E. Maslar, E.S. Windsor,* NIST

A nickel-chromium-iron alloy (Inconel 600) was exposed to water at elevated temperatures and pressures (approaching conditions of the critical point of water). This alloy is used in boiler systems and the mechanisms of corrosion and failure are of interest. The water temperatures and pressures were selected to simulate conditions to which this alloy might be exposed during operation. Two coupons were exposed under slightly difference conditions and differences in degree of corrosion were observed. While the alloy composition is well known, the composition of the corrosion layer depends strongly on exposure conditions. Auger electron spectrometry was applied to help investigate the composition of the corrosion layer. The discontinuous nature of the oxidation layer and the proximity to the unoxidized substrate make this a challenging analysis. Auger analysis is complimented with energy dispersive spectrometry, and focused ion beam techniques to solve this complicated analysis problem.

AS-MoP16 Electronic Structure of Rare-Earth Oxoborates: A Photoemission Investigation*, **A.J. Nelson**, J.J. Adams, K.I. Schaffers,* Lawrence Livermore National Laboratory

Calcium's rare-earth (R) oxoborates are nonlinear optical materials with general composition Ca@sub 4@RO(BO@sub 3@)@sub 3@ (R@super 3+@ = La, Sm, Gd, Lu) that have potential for high-average power laser frequency conversion and intra-cavity doubling. X-ray photoemission was applied to study the valence band electronic structure and surface chemistry of these novel materials and their rare-earth oxide model compounds. Core-level and valence band results for the rare-earth oxides La@sub 2@O@sub 3@, Sm@sub 2@O@sub 3@, Gd@sub 2@O@sub 3@, and Lu@sub 2@O@sub 3@, were applied to the interpretation of the photoemission spectra of select oxoborate crystals. Specifically, high resolution photoemission measurements on the La and Gd 3d and 4d, Ca 2p, B 1s and O 1s core lines and valence band were used to evaluate the surface and near surface chemistry of lanthanum calcium oxoborate (LaCOB) and gadolinium calcium oxoborate (GdCOB). Results for these oxoborate crystals revealed that the occupied states exhibit a high degree of mixing between the p-f bonding-antibonding states. In addition, general treads in the 3d and 4d core-level line shapes and occupied 4f valence band states of the rare-earth oxide model compounds are best understood in terms of final state effects. This work was performed under the auspices of the U.S. Dept. of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

AS-MoP17 Photoelectron Spectroscopy Study of the Aging and Plasma Treatments Effects on PECVD a-SiC:H Films for Advanced Interconnects*, **V. Jousseaume**, O. Renault,* CEA-DRT-LETI, France*; G. Passemard,* ST-Microelectronics, France

The ageing of amorphous hydrogenated SiC (a-SiC:H) films grown by PECVD and used as potential low k dielectric barrier materials in advanced interconnects was investigated by x-ray photoelectron spectroscopy. Very thin layers (20-60 nm) and a special sample holder were used in order to minimize detrimental charging effects during analysis. It is shown that ageing on non-treated films proceeds by the introduction of up to 20at.% of oxygen into the film after 15 days of air exposure in the clean room, and that O is present in relatively high concentration at the very early stages of air exposure@footnote 1@. By XPS is evidenced the benefits of both He and H2 plasma treatments in term of drastic limitation of the reoxidation upon ageing, with an atomic percentage of O being stable at around 7at.% after 15 days. At the same time, on untreated samples, the Si/(Si+C) ratio is remaining constant and both Si2p and C1s core-level profiles show up a constant evolution as a function of ageing time, with a decrease of the relative intensity of Si-C bonds and an increase of oxycarbide and C-C, C-H groups. This evolution will be compared with the case of plasma treated samples and possible mechanisms of ageing will be proposed taking into account results from FTIR analysis, stress and dielectric constant measurements@footnote 2@. @FootnoteText@ @footnote 1@McCurdy et al., J. Electrochem. Soc., 145-9 (1998) 3271).@footnote 2@Jousseaume et al., E-MRS Meeting 2004.

AS-MoP18 Thermally Nitrided Stainless Steels for Polymer Electrolyte Membrane Fuel Cell Bipolar Plates: Beneficial Modification of Passive Layer on AISI446*, **H.M. Meyer III**, M.P. Brady, K.L. More, B. Yang,* Oak Ridge National Laboratory*; H. Wang, J.A. Turner,* National Renewable Energy Laboratory

Proton exchange membrane fuel cells (PEMFCs) are of great current interest for power generation due to their high efficiency and environmentally friendly, near-zero emissions. Since cost is critical, metal alloys would be ideal as bipolar plates but suffer from inadequate corrosion behavior due to high electrical resistance by the formation of surface oxides or degrade cell performance by contaminating the membrane with metal ions. Recently, it was discovered that thermally grown Cr nitrides (CrN/Cr2N) on a model Cr-bearing alloy, Ni-50Cr (wt%), show great promise for corrosion resistance and electrical conductivity in PEMFC bipolar plate environments @fototnote 1@. Work is ongoing to form similar nitride surfaces on less expensive Ni-Cr and Fe-Cr base alloys. This poster describes an effort to use a relatively inexpensive ferritic stainless steel (AISI446 MOD-1) as bipolar plate material and specifically looks at its surface chemistry, corrosion resistance, and interfacial contact resistance. Thermal nitridation for 2 h at 1100ÂºC resulted in little nitrogen uptake and a tinted surface. Analysis by SEM, XPS, and AES suggests a complex heterogeneous modification of the native passive oxide film by nitrogen, rather than the desired micron range thick exclusive Cr-rich nitride layer. Surprisingly, this modification resulted in both good corrosion resistance under simulated cathodic and anodic conditions and low ICR, well over an order of magnitude lower than the untreated alloy@footnote 2@. Details of the nitrided surface chemistry of this alloy will be presented. @FootnoteText@ @footnote 1@ M.P. Brady, K. Weisbrod, I. Paulauskas, R.A. Buchanan, K.L. More, H. Wang, M. Wilson, F. Garzon, L.R. Walker, Scripta Materialia, 50(7) pp.1017-1022 (2004).@footnote 2@ H. Wang, M P. Brady, K.L. More, H.M. Meyer III, and J. A. Turner. Submitted to Journal of Power Sources.

AS-MoP19 Preparation and Lithography of Monolayers on Silicon Surface and Their Molecular Recognition*, **Y. Takahashi**,* Waseda University, Japan*; N. Shirahata,* National Institute for Materials Science, Japan*; A. Hozumi,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Asakura,* Waseda University, Japan*; T. Yonezawa,* University of Tokyo, Japan

Functionalization of hydrated silicon surface is a starting stage in the development of molecular, biomolecular and semiconductor devices. Refluxing of 1-alkene under nitrogen with H-terminated Si gives an uniform Si-C linked monolayer with atomically flatness through thermal hydrosilylation. We have reported that the monolayer can be prepared from a dilute solution of 1-alkene (< 1 wt%) and even from powder of 1-alkene molecules. This basic finding that the monolayer can be prepared from the powder implies that solid materials, including those with exceedingly high melting points or no melting points, have the potential to be transformed into monolayers directly bonded to inorganic substrates, with the only limitation being that the material must be soluble into any kinds of solvents. The carbohydrate monolayer recognizes the specific protein molecules selectively. Lithography of such monolayer can be done by UV-light irradiation. Furthermore, the particle monolayer of alkenethiol-stabilized gold nanoparticles were also be anchored onto silicon by similar reaction. These findings will promise that individual nanoscale materials can be manipulated based on monolayer formation mechansm.

AS-MoP20 Importance of Binding Energy Reference Materials for Understanding the Chemistry of Oxidized-Iron Arsenic-Adsorbing Materials*, B.M. Sass,* Battelle Columbus; ***M.H. Engelhard**, D.R. Baer,* Pacific Northwest National Laboratory

Arsenic as a contaminant in drinking water is a growing problem around the world. Consequently many research and commercial efforts are being made to develop low cost and effective means for producing acceptable quality drinking water. Iron oxide based sorbing minerals are now available commercially. However, the effectiveness, lifetime and ability to recycle these materials are not adequately understood. The extent of arsenic sorption and the chemical nature of the sorbed species are important to understanding the chemistry that take place on the surface and the long term effectiveness. We have used XPS to measure the arsenic coverage on the mineral surfaces and to examine arsenic chemical state. Because of the limited amount of arsenic oxidation state data in general, the variability of binding energies observed in the existing data, and the lack of data for arsenic sorbed onto oxidized iron phases, to interpret our data it was necessary to examine As(III) and As(V) oxides as well as ferric arsenite and ferric arsenate compounds. Based on these references the arsenic sorbed onto the commercial sorbers was found to be mostly As(V) in the conditions examined.

AS-MoP21 Analysis of Leed Images to Obtain Surface Geometries of Amines and Alcohols Adsorbed on the Si(100)-2x1 Surface*, **J.K. Dogbe**, S.M. Casey,* University of Nevada, Reno

Image analysis of low-energy electron diffraction (LEED) intensity vs. voltage (IV) curves was used to analyze the surface geometries of amines and alcohols adsorbed on the Si(100)-2x1 surface. Clean silicon and ammonia-covered surfaces were used as calibration systems. The data from these surfaces compare well within experimental uncertainties. Results to be presented include the dimethylamine, trimethylamine and ethanol-covered surfaces. These results will be compared to computational treatments of probable reaction pathways of these adsorbates on silicon using the cluster models of the surface. Also to be presented will be comparisons of results for these reactions from slab models of the surface.

AS-MoP22 Surface Planarization Characteristics of WO3 Thin Film for Gas Sensing*, W.S. Lee, **P.J. Ko**,* Chosun University, South Korea*; Y.J. Seo,* DAEBUL University, Korea, South Korea

There has been an increasing interest in the material and electrical properties of inorganic compound that are insulators at low temperature, but are good conductors at high temperature. In particular, n-type semiconductors such as SnO2, WO3, TiO2 and ZnO have extensively been used for detecting reduction gases. For the applications of gas sensors, it is necessary to have a microstructure with small grain size yielding large ratio of the surface area to the bulk. Also, the surface roughness deteriorates light reflection, pattern resolution, and device performance because they are dependent on surface morphology or roughness. Therefore, it is important to control the microstructure and surface morphology for the advanced sensor application. Chemical mechanical polishing (CMP) process is a useful guideline for improving the surface roughness. In this paper, we investigated the CMP effects on the surface morphology of WO3 thin films prepared by RF sputtering system. In order to compare the polishing characteristics of WO3 thin film, we discussed CMP removal rate (RR) and within-wafer non-uniformity (WIWNU%), particle size distribution, and the microstructures of surface and cross-sectional layer by atomic force microscopy (AFM) analysis. And the effects of added oxidizer contents on the WO3 CMP characteristics were investigated to obtain the higher removal rate and lower non-uniformity. This work was supported by a Korea Research Foundation grant (KRF-2002-005-D00011).

AS-MoP23 Scanning Capacitance Microscopy Study on the Stability of the Electrical Junctions Formed by Spike Annealing and Rapid Thermal Annealing*, **M.-N. Chang**, C.-Y. Chen,* National Nano Device Laboratories, Taiwan

Scanning capacitance microscopy (SCM) has been widely used to profile two-dimensional carrier distribution and examine the electrical junctions of silicon-based devices. Ion implantation combined with proper annealing treatments is indispensable to produce a needed electrical junction. In general, the annealing treatments can be rapid thermal annealing (RTA) or spike annealing (SA) at high temperature. Due to the photoperturbation effects on SCM, there are many difficulties in employing SCM to investigate the temperature influence on electrical junctions. In this work, we have provided a reliable method to control the photoperturbation levels on the studied samples and employed low-photoperturbed SCM, operated under the same photoperturbation levels, to study the stability of the electrical junctions formed by RTA and SA. Studied samples were p@super +@/n junctions formed by BF@sub 2@@super +@ implantation at low energies. RTA and SA processes were performed at 1050 °C in N@sub 2@ ambient. The width and pitch of the designed grating pattern are 0.8 and 2 @micro@m, respectively. The differential capacitance images clearly show that post-SA and -RTA furnace annealing at low temperatures can induce the electrical junction narrowing. With secondary ion mass spectroscopy, it is further revealed that the junction narrowing may occur even if atomic diffusion is negligible. The experimental results indicate that point defect generation/recombination associated with dopant deactivation plays an important role of junction width modification during the following low temperature processes. According to this study, the electrical junction formed by high temperature annealing is unstable. The physical mechanism of junction width variation induced by low temperature processes will be discussed in depth.

AS-MoP24 XPS Analysis Under External Stimuli*, **S. Suzer**, U.K. Demirok, G. Ertas,* Bilkent University, Turkey

Earlier, we demonstrated that, by applying external voltage bias to the sample rod while recording XPS spectra, it was possible to influence the measured binding energy differences by controlling the partial charging/discharging of different surface layers or domains either by electrons created from a filament, or by stray electrons within the vacuum system stemming form X-ray tube, vacuum gauges, etc.[1, 2]. We had used this to separate otherwise overlapping XPS peaks belonging to different surface features.[3] Later, we expanded it to extract time-dependent information. [4] In this contribution, we will present our extended investigation of different surface structures like Au nanoclusters deposited on SiO2 substrates or thin organic layers of various thickness, etc., using different external voltage stimuli over other external elements like resistors, capacitors for extracting information related with the dielectric properties of surface structures and probing nanocluster-surface interactions. @FootnoteText@ [1] B. Ulgut, and S. Suzer, J. Phys. Chem. B 107, 2939 (2003). [2] F. Karadas, G. Ertas, and S. Suzer, J. Phys. Chem. B 108, 1515 (2004). [3] S. Suzer, Anal. Chem. 75, 7026 (2003). [4] U. K. Demirok, G. Ertas, and S. Suzer, J. Phys. Chem. B 108, 5179 (2004).

Applied Surface Science
Room 210A - Session AS-TuM

Electron Spectroscopies

Moderator: R. Haasch, University of Illinois, Urbana

8:20am **AS-TuM1 Light Induced Chemically Resolved Electrical Measurements (LICREM) in XPS: Anomalous Photoresponse of CdSe Nanoparticle Films***, **H. Cohen**, S. Sarkar, G. Hodes,* The Weizmann Institute of Science, Israel

A novel method, based on electrically and optically stimulated XPS, is applied to thin overlayers of CdSe nanoparticles. Negative differential resistance is observed in the dark chemically resolved electrical measurements (CREM)@super1@. The photoresponse under variable electrical conditions shows that the system can operate in two modes, differing in the direction of photocurrent. A phenomenological model is provided, explaining the anomalous photoresponse by means of competing charge trapping mechanisms, which allow real-time shaping of space charge and, hence, of the local electric fields. @FootnoteText@ @footnote 1@ H. Cohen, Condensed Matter Archive 031147, (Nov. 20, 2003).

8:40am **AS-TuM2 Validation of Information Gained from the XPS Survey Scan***, **J.E. Castle**, C. Lavie-Compin,* University of Surrey, UK

Members of the 34th IUVSTA workshop @footnote1@ reported an â?oimplementable protocol for the collection and analysis of a standard survey scan; allowing extraction of the maximum available informationâ?. This information might then guide the next steps in sample analysis or might be sufficient in itself. Autonomous extraction of information required in corrosion science has been discussed @footnote2@. Here we compare data obtained from the survey scan with high resolution scans for four Cu/Ni alloys. They were examined: a) ion-etched ; b) carrying the air-formed oxide and contamination; c) after oxidation in air at 100ÂºC; and d) as c) with a brief ion-etch. The survey scan was used to determine key data including: a) testing for adventitious contamination by organic molecules @footnote3@; b) the thickness of the contamination layer; c) the apparent surface composition, corrected for the influence of contamination; d) the surface enrichment factor and enrichment rank; e) the principle chemical species in the surface, determined by the Auger parameter, and/or the presence of satellites @footnote4@; f) the thickness of the oxide, determined by peak fitting regions taken from the survey scan. The comparison enables the value of guidance given by the survey scan and the extent to which it is sufficient for purpose, to be assessed. @FootnoteText@ @footnote1@ J.E.Castle and C.J.Powell â?oReport on the 34th IUVSTA Workshop â?~XPS: from spectra to results â?" towards an expert systemâ? Surf.Interface Anal. 36 pp225 - 37 (2004) @footnote2@ J.E.Castle â?oModules for an XPS Expert System: Applications in Corrosion Scienceâ?, QSA Symposium: AVS 50th Meeting, Baltimore 2003. @footnote3@ J.E.Castle and M.A.Bakerâ?oThe Feasibility of an XPS Expert System Demonstrated by A Rule Set for Carbon Contaminationâ? J. Elec Spec Related Phenomena, 105 pp245 - 256 (1999) @footnote4@ J.E.Castle â?~A Wizard Source of Expertise in XPSâ?T Surf.Interface Anal. 33 pp 196 - 202 (2002).

9:00am **AS-TuM3 Extensions of Photoelectron Spectroscopy to the Study of Nanoscale Systems***, **R.L. Opila**, K. Demirkan, A. Mathew,* University of Delaware **INVITED**

Photoelectron spectroscopy (PES) is a very powerful probe of elemental composition and structure at nanometer length scales. PES of core levels can identify which atoms are present, their relative concentrations, and their chemical bonding. PES of the valence levels yields more insight into the chemical bonding. This technique achieves its surface sensitivity from the charge on the photoelectron and its high probability of inelastic collisions. This complication provides both complications and opportunities. First, the photoelectrons are not collected as a linear function of depth, but approximately by an exponentially decreasing function of depth, where the decay length is given by an average of the emission depth distribution function. Collecting the emitted photoelectrons over several angles changes the sampled range of depths. Several algorithms have been proposed that permit the variation in intensity as a function of collection angle to be converted to elemental concentration as a function of depth. We will discuss a maximum entropy algorithm and show its application to study of high-k dielectrics as gate oxides for transistors. The charge on the photoelectrons also samples the local electronic charges that might be present. Through Coulombic interaction with these charges, their kinetic energy is shifted. It is possible to determine the amount of fixed charge present at a chemical interface by determining the relative shift between the photoelectrons emitted from overlayer and those from the substrate. Examples of interfacial charge, including high-k oxide/Si and Al2O3/Al, will be discussed.

9:40am **AS-TuM5 XPS Chemical Depth Profiling Using C@sub 60@ Ion Beams***, **N. Sanada**, A. Yamamoto, H. Iwai,* ULVAC-PHI, Inc., Japan*; J.F. Moulder,* Physical Electronics*; R. Oiwa, Y. Ohashi,* ULVAC-PHI, Inc., Japan

XPS is one of the most common analytical techniques which can be applied to the chemical analysis of a wide range of materials such as organic polymers, ceramics, metals and semiconductors. However, depth profiling with XPS requires sputtering with ion beams, which are well known to induce sample damage and have the constraint of sample chemical information being lost. Recently, we have applied a buckminsterfullerene (C@sub 60@) ion beam for depth profiling during XPS analysis[1]. A practical sputter rate of 2.4 nm / min. for SiO@sub 2@ was obtained with a sputtered area of 5 mm x 5 mm using a 5 kV C@sub 60@ ion beam. Extremely low sputtering degradation of organic polymers such as polytetrafluoroethylene[1], a polyester, a gelatin, and a latex [2] were observed under these conditions. In the meantime, the carbon contaminants derived from the C@sub 60@ ion beam varied under different sputter conditions. We studied the beam condition using a thermally oxidized SiO@sub 2@ film sample to minimize carbon residue determined by XPS. The quantities of carbon residue in the SiO@sub 2@ film reduced from 85 at% to 0.2 at% as the beam energies were modified from 2 keV to 30 keV. The incidence angle of the ion beam also affected the carbon residue in the film. XPS chemical depth profiling with C@sub 60@ sputtering applied to organic thin films will be discussed in this presentation. [1] N. Sanada et al., Surf. Interf. Anal., 36, 280 (2004). [2] N. Sanada et al., Extended Abstracts 51st Spring Meeting, 2004; Jpn. Soc. Appl. Phys. Rel. Soc. 29p-YD2.

10:00am **AS-TuM6 X-Ray Photoelectron Spectroscopy of Rubber Compounds: Temperature Dependence and Crosslink Distribution***, **G.E. Hammer**,* The Goodyear Tire & Rubber Company

Rubber compounds are complex mixtures of ingredients, including many mobile and volatile species. Exposure to the ultra high vacuum environment common to surface analytical instruments can therefore cause significant changes in a rubber surface and produce misleading and even erroneous results. In this work it has been shown that stable, representative x-ray photoelectron spectra could be obtained if the specimen was pre-cooled below a compound-dependent maximum temperature before exposure to the vacuum environment. Maximum temperatures were found to be -50°C and -70°C for two typical tire rubber compounds, a wire adhesion formulation and passenger tire tread, respectively. Effects of specimen preparation were further investigated. High resolution x-ray photoelectron spectra of specimens pre-cooled to -85°C and analyzed at -140°C indicated a correlation between the sulfur peak positions and the length of sulfur crosslinks in the rubber. Specifically, a linear relationship was found between sulfur 2p binding energy and the percentage of polysulfide crosslinks as determined by standard bulk solvent swelling analysis for three different rubber compounds based on two different polymers.

10:20am **AS-TuM7 Monte Carlo Simulations of Electron Backscattering from Surfaces in Scanning Auger Microscopy***, **C. Powell**,* NIST*; A. Jablonski,* Institute of Physical Chemistry, Poland

Monte Carlo (MC) simulations are useful for calculating signal intensities in AES because multiple-scattering events can be conveniently included. In this contribution, a new MC algorithm for AES is presented in which recent advances in knowledge of electron transport are incorporated. Differential cross sections for elastic scattering were obtained from a NIST database.@footnote 1@ The inelastic-scattering events were described by energy-loss functions derived from optical data, and "recommended" inelastic mean free paths for energies up to 10 keV were utilized.@footnote 2@ The empirical formula of Casnati et al.@footnote 3@ was used to describe inner-shell ionization cross sections. Particular care was taken in preparing the random number generators for simulation of the angular and energy distributions after elastic- and inelastic-scattering events because of numerous sharp features (e.g., deep minima) in the relevant probability distributions. We report new calculations of the backscattering factor (BF) for Auger transitions of Si, Cu, Ag, and Au as a function of primary energy, and find that the BF depends also on the Auger-electron emission angle. We investigated the radial distribution of emitted Auger electrons from a thin Cu film on Si and Au substrates. Due to the effects of electron backscattering, the radius of the analysis area depends considerably on the primary energy and the substrate, and can be much larger than the radius of the primary beam. We also examined the effects of backscattering on Auger line scans in the vicinity of the edge of a Cu film on Si and Au substrates. @FootnoteText@ @footnote 1@A. Jablonski, F. Salvat, and C. J. Powell, NIST Electron Elastic-Scattering Cross-Section Database, Version 3.1, SRD Database 64 (2003). @footnote 2@C. J. Powell and A. Jablonski, J. Phys. Chem. Ref. Data 28 (1999) 19. @footnote 3@E. Casnati, A. Tartari and C. Baraldi, J. Phys. B 15 (1982) 155.

10:40am **AS-TuM8 Round Robin Study of Evaluation of Electron Beam Damage of SiO2/Si in Auger Microprobe Analysis*, S. Tanuma,*** *T. Kimura,* National Institute for Materials Science (NIMS), Japan*; S. Hashimoto,* Kokankeisoku, Japan*; M. Inoue,* Setsunan University, Japan*; M. Suzuki,* ULVAC-PHI, Inc., Japan

Auger electron spectroscopy (AES) is routinely employed for characterization of wafers at various stages of device fabrication, for the identification of defects, and for process development. A major limitation of AES, however, is the fact that the incident electron beam can initiate unwanted chemical changes. While many investigations have been made on electron irradiation damage of silicon dioxide during analyses by Auger electron spectroscopy (AES), it is very complicated or tedious to determine the critical dose for such damage from intensity changes of the silicon L3VV Auger spectrum versus irradiation time. Then, we plan to make an accurate and quantitative method of the evaluation of surface damage on the specimen caused by the electron beam irradiation. We have made measurements of the Si L3VV spectrum on SiO2 (100nm)/Si and SiO2 (10nm)/Si specimens versus electron dose at 3, 5, 10 and 15 keV. The measurements were carried out for a wide range of the total irradiation dose: 0.001 - 150 C/cm2. We found that the peaks to background intensities of Si LVV metallic peaks are changed due to the increase of measurement time (or total electron dose). We have also developed an equation that represents the Si LVV metallic peak intensities as a function of total electron dose, based on the two-step decomposition model for SiO2. This method has two parameters that represent the EDCS of SiO2 and SiO, respectively. Form the curve fit of the proposed equation to the measured Si LVV metallic peak intensities, we can determine the critical dose of electrons for SiO2 decomposition quantitatively.

11:00am **AS-TuM9 Performance of a High throughput TOF-HREELS Analyzer*, Z. Yang,*** University of Maine*; R.H. Jackson,* Stillwater Scientific Instruments*; P.H. Kleban, B.G. Frederick,* University of Maine

Despite tremendous advances in monochromators, the efficiency of conventional analyzers in high resolution electron energy loss spectrometers (HREELS) is poor (~ 0.1%) due to the serial nature of the dispersive analyzer: only 1 out of typically 2000 energy channels can be measured at any one time. Pseudo-random binary sequence modulation is a method of multiplexing in the time domain to increase the throughput of the analyzer to 50%. We have combined PRBS modulation in an electron time-of-flight analyzer with maximum likelihood signal recovery methods to decrease data acquisition times from hours per spectrum to a few minutes, while maintaining resolution in the 2-4 meV range. We will present results from several samples that demonstrate the capabilities of the state-of-the-art time-of-flight TOF-HREELS instrument. Data measured on azimuthally oriented polytetrafluoroethylene (Teflon) films reproduce the complex spectral features and achieve resolution comparable to spectra measured with the conventional instrument. Results on the c(2x4) O/Pd(110) surface, in which the intensity of the oxygen-metal stretch relative to the elastic peak is < 0.1%, demonstrates the large dynamic range that has been achieved, again with resolution below 3 meV off the surface. Similar performance is obtained for CO/Pd(110), in good agreement with recently published spectra by Kato, et al.@footnote 1@. @FootnoteText@ @footnote 1@ Kato, H.; Okuyama, H.; Ichihara, S.; Kawai, M.; Yoshinobu, J. J. Chem Phys 2000, 112, 1925.

11:20am **AS-TuM10 Oxygen Environmental Electron Spectroscopy and Microscopy: A New Concept for Reducing Harmful Electron Beam Effects on Insulating Samples*, Y. Ji,*** *H. Guo,* Beijing University of Technology, China*; V. Kempter,* Technische Unviversität Clausthal, Germany

Charging phenomena occur on insulating surfaces in many types of surface analysis techniques. In the case of electron spectroscopy and microscopy using an electron beam as probe, the charging phenomena can seriously distort the spectra and images, even make the analysis impossible. In addition, the electron beam can change the surface composition through electron stimulated desorption (ESD) and electron stimulated adsorption (ESA). These effects on oxide samples in Auger electron spectroscopy analysis can be markedly reduced or eliminated in oxygen pressures @<=@ 6*10@super -@@super 6@ Pa. Using oxygen environment to reduce the surface charging-up is based on a novel concept: Reducing the charging effects through eliminating electron traps resulting from electron beam damage, specifically, the ESD of surface oxygen. This is a breakthrough in the understanding of the charging mechanism, as the existing methods for reducing charging-up are mostly based on considerations such as increasing the surface conductivity by coating a conducting layer, increasing the secondary electron yield by applying an additional low energy electron beam, neutralizing the negative surface charges by providing positive charges, increasing the bulk conductivity by sample heating, etc. The significance of this method is that it can also compensate the depletion of the surface oxygen due to ESD and eliminate the surface contamination from background adsorption; it is applicable to other analysis techniques such as scanning electron microscopy, electron probe microanalysis, electron diffraction, electron energy loss spectroscopy.

Applied Surface Science
Room 210A - Session AS-WeM
Chemometric Analysis of Spectral or Image Data; XPS/TOF-SIMS Applications

Moderator: J.E. Fulghum, The University of New Mexico

8:20am **AS-WeM1 Angle-resolved X-ray Photoelectron Imaging of Heterogeneous Polymer Samples***, **K. Artyushkova**, J.E. Fulghum,* The University of New Mexico

ARXPS has been widely used for thickness calculations, discerning molecular orientation, and estimating both surface enrichment and concentration gradients. For multicomponent heterogeneous samples not only the average concentration but morphology and chemical heterogeneity are important. In this work we demonstrate the results of combining ARXPS and imaging for analysis of polymer blend samples. Challenges in combining the two approaches include locating the same area for image acquisition at multiple take-off angles, the small depth of focus in imaging mode, and the geometrical transformation of images with changing take-off angle. The conversion of the original photoelectron images to a volume representing the top 3-10 nm of the polymer blend includes principal component analysis, spatial image transformation to correct for geometry or image warping, automatic image registration, mapping images to concentration with the assistance of AR small area spectroscopy, image morphing and visualization. AR images were used to create volumes from the top 3-10 nm of blends of polyvinylchloride (PVC) and polymethylmethacrylate (PMMA) or polystyrene (PS). These volumes allow for the visualization and estimation of the degree of surface segregation and separation of polymer phases. This work has been partially supported by NSF CHE-0113724.

8:40am **AS-WeM2 Detection of Small Chemical Changes on Liquid Crystal-Aligning Polymer Surfaces using Multivariate Data Analysis of XPS Spectra***, **S. Pylypenko**, K. Artyushkova, J.E. Fulghum,* The University of New Mexico

Ion beam alignment of liquid crystals is one of several non-contact methods under investigation as a substitute for mechanical rubbing. The characterization of Ar+ ion beam modified polymers is required in order to understand the macroscopic and microscopic alignment mechanisms. Polymer alignment layers, including polyimide and polystyrene, were studied using X-ray Photoelectron Spectroscopy (XPS) to characterize chemical changes and the surface anisotropy of the alignment substrate. XPS spectra were acquired from samples before and after bombardment, after exposure to the atmosphere, and after 90 degree rotations. XPS spectra of the polymers are dominated by changes resulting from Ar+ ion beam exposure, but also contain smaller changes related to chemical anisotropy. The effect of surface oxidation resulting from the high reactivity of the polymer surfaces after bombardment also must be taken into consideration when interpreting the spectra. We used multivariate analysis to differentiate between chemical changes from ion beam bombardment and oxidation versus the small changes due to chemical anisotropy created by the ion bombardment. Spectra manipulation, including subtraction, and multivariate analysis using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR) allowed us to extract information about small changes due to chemical anisotropy. The anisotropy, and associated liquid crystal alignment, result from selective destruction of the weakest bonds relative to the direction of ion beam bombardment.

9:00am **AS-WeM3 Identifying Surface Chemical Changes with XPS Spectral Imaging and Multivariate Statistical Analysis@footnote 1@***, **D.E. Peebles**, J.A. Ohlhausen, K.R. Zavadil, M.R. Keenan, P.G. Kotula,* Sandia National Laboratories

Imaging X-ray Photoelectron Spectroscopy (XPS) allows the distribution of elements and chemical states to be mapped across a surface region of interest. Conventional use of XPS mapping involves utilizing images acquired at peak intensities for chemical species of interest with the subtraction of a suitable background image off the peak. Both peak and background image energies need to be determined from a prior spectrum taken from the imaged region to insure optimal energy selection. While this allows differentiation of chemical states, image contrast and resolution may be poor, especially for overlapping spectral peaks. A more complete and definitive picture of the distribution of chemical species across the surface may be obtained by acquiring a series of images over an energy range that covers the peaks of interest. This generates a very large amount of data that must be processed and correlated, generally with some form of multivariate statistical analysis. Many types of multivariate statistical analyses require user input for the number of species present and their general lineshape. Others produce non-physical spectra that may be difficult to interpret. Multivariate statistical analysis methods developed at Sandia National Laboratories facilitate the rapid analysis of the large quantities of data produced by spectral imaging in an efficient manner without user bias or input. The use of these methods for XPS spectral images to detect changes in chemical state will be demonstrated. In particular, examples illustrating the ability of these techniques to resolve overlapping peaks and reveal correlated species will be included. @FootnoteText@ @footnote 1@ This work was completed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:20am **AS-WeM4 Algorithm for Improved XPS-Imaging***, **S. Tougaard**,* University of Southern Denmark, Denmark

Non-destructive XPS-imaging of surfaces is based on analysis of peak intensities. It is however well known that XPS-quantification from the peak intensity leads to huge uncertainties because the measured intensity depends strongly on the depth distribution of atoms. The problem was basically solved by developing models for the detailed analysis of the energy distribution of emitted electrons leading to algorithms summarized in.@footnote 1@ The validity of these algorithms have been extensively tested experimentally and found to be able to accurately determine both the quantitative amount of atoms as well as their in-depth distribution within the outermost ~ 5-10 nm of surfaces. Practical application of these algorithms has increased after ready to use software packages were made available and they are now used in labs worldwide. These software packages are easy to use but they need operator interaction. They are not well suited for automatic data processing and there is a need for simplified strategies that can be automated and used in e.g. XPS-imaging where the huge amount of data hinders manual data analysis. In this paper we study a very simple algorithm that automatically takes the XPS-peak attenuation effect into account@footnote 2@. The algorithm is less accurate than those in@footnote 1@ but it is substantially more accurate than using peak intensities and it is well suited for automation. It gives the amount of atoms within the outermost ~ 3IMFP with a good accuracy and it gives also a rough estimate for the in-depth profile. In the talk, the validity of the simple algorithm is tested on several experimental systems and the results are compared to analysis of the same samples quantified by more accurate methods. The algorithm seems promising for significant improvements in XPS-imaging. @FootnoteText@ @footnote 1@ S. Tougaard, J. Vac. Sci. Technol. A14, 1415 (1996); see also www.quases.com@footnote 2@ S. Tougaard, J. Vac. Sci. Technol. A21, 1081 (2003).

9:40am **AS-WeM5 Chemometric Techniques for Two-way, Three-way and Higher-order Image Data***, **J.M. Shaver**,* Eigenvector Research, Inc., US*; B.M. Wise,* Eigenvector Research, Inc. **INVITED**

Historically, analytical instrumentation would measure a single response such as intensity or counts as a function of a single parameter such as incident energy (e.g. a spectrum). When this response is measured for a range of samples, one obtains "two-way" data. Each sample gives a single vector of responses. A wide variety of numerical analysis techniques exist for performing quantitative and qualitative analyses of two-way data. However, an increasing number of instruments measure response as a function of multiple parameters such as position on the sample, incident energy, and energy of response. Add to these the measurement of multiple samples and the data can become quite complex with respect to relationships between parameters. One method of analyzing such data is to focus on only one parameter at a time (sample vs. incident intensity) or, alternatively, to ignore the relationship between parameters and string the data into one long series of responses per sample. An more sophisticated approach arranges the data into a multi-way array which can be analyzed for relationships between controlled parameters as a function of sample. This often allows improved accuracy and specificity and, in some cases, is even easier to analyze because of the interrelationships. This paper will discuss the concept of multi-way data and some of the issues associated with its analysis, with particular note to multi-way spectroscopic images.

10:20am **AS-WeM7 Maximum Likelihood Principal Component Analysis of ToF-SIMS Spectral Images***, **M.R. Keenan**,* Sandia National Laboratories

Many modern surface analytical instruments are able to acquire huge amounts of data in the form of spectral images. ToF-SIMS, for instance, can easily generate a complete mass spectrum at each point in a 2D or 3D spatial array. The challenge for the data analyst, then, is to garner the analytically useful information from the overwhelming quantity of raw spectral data. Factor analysis techniques such as Principal Component Analysis (PCA) have proven quite useful in this endeavor. Standard PCA, however, assumes that noise in the data is uniform, that is, that it does not depend on the magnitude of signal. This is clearly not correct for methods that rely on particle counting where the noise is governed by Poisson statistics. In this case, properly accounting for heteroscedasticity is essential to extracting the chemical information into a minimum number of factors while maximally excluding noise. Maximum Likelihood PCA (MLPCA) is one approach to addressing this issue. MLPCA can, in principle, incorporate a separate uncertainty estimate for each individual observation in a data set. This paper will present a MLPCA analysis of a simple and intuitive ToF-SIMS spectral image. The results show that there is a tradeoff between the number of uncertainty parameters included in the model and the quality of each and, in fact, using poor estimates may be worse than doing nothing at all. The best results were obtained by using a low-rank approximation to the noise rather than individual estimates. MLPCA will also be compared with an optimal scaling approach. For the particular example given, the added benefits of MLPCA probably do not outweigh the greatly increased computational demands of the technique. This work was completed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **AS-WeM8 AXSIA Analysis of TOF-SIMS Spectral and Image Series Data@footnote 1@**, ***J.A. Ohlhausen***, *K.R. Zavadil, R.D. Kilgo,* Sandia National Laboratories

AXSIA (Automated eXpert Spectral Image Analysis), a patented multivariate approach invented at Sandia National Laboratories, is used to provide comprehensive analysis of spectral series and spectral image series. We directly compare spectra from many different samples (spectral series) and compare spectral images from different specimens or locations (spectral image series) using this statistical approach. This method of analysis provides full spectral separation of distinct components present within the system of interest. Component variation is expected with fragmentation changes resulting from aging, contamination, concentration, molecular orientation, and chemical reaction. We use spectral series analysis to understand how component variation might be impacted by monolayer deposition and coverage. Spectral series analysis with AXSIA shows promise in extracting a more quantitative determination of the effect of saturation coverage and molecular orientation on fragmentation patterns. We have also been able to process large, complex image datasets containing a number of analysis areas at once. By using a technique of merging multiple datasets into one large dataset, a direct comparison of analysis locations is made. The relative amount of contaminant and substrate species as a function of handling and processing conditions are determined. The effects of processing and handling are readily extracted in this chemical system because all data is processed at once. As a result, the information contained in the component analysis is complete and comprehensive. @FootnoteText@ @footnote 1@This work was completed at Sandia National Laboratories, a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:00am **AS-WeM9 ToF-SIMS as an Important Tool for Fuel Characterization: A Chemometrics Study**, ***G. Jiang***, *D. Stone, L. Baxter,* Brigham Young University; *B.J. Tyler,* University of Utah; *M.R. Linford,* Brigham Young University

The combustion of coal and biomass provides a significant amount of the energy needs of the world. As expected, there is a series of standardized tests for characterizing these materials. However, these time-consuming analytical methods do not generally provide the chemical information that is necessary to predict and better understand important problems such as NO formation and soot production. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is one of the most powerful surface analytical methods in existence. Here we investigate the possibility of using a single ToF-SIMS analysis to characterize coal and biomass as a replacement for many of the tests that currently need to be performed on each sample. But more importantly we look to ToF-SIMS as a tool that can provide data that is rich in chemical information. To handle the enormous quantities of data that are produced by ToF-SIMS it has become increasingly common to use chemometrics methods such as PCA, PLS, and cluster analysis. Here we report a chemometrics study of ToF-SIMS spectra of a series of coal and biomass samples. As expected, PCA of ToF-SIMS spectra of coal and biomass show these classes of materials to be distinctly different. In particular, scores and loadings plots of coal and biomass ToF-SIMS spectra show that the coal spectra are dominated by inorganic ions, while the biomass spectra are dominated by organic ions. We also note that data preprocessing has a significant impact on the resulting PCA, where more information appears to be available from the data when normalization and standardization are applied. PLS of biomass data shows excellent agreement between the nitrogen content of these fuels and the ToF-SIMS spectra. In summary, these multivariate analyses help build the case for ToF-SIMS as a useful and powerful tool for fuel analysis.

11:20am **AS-WeM10 A Chemometrics Analysis of ToF-SIMS Spectra of Monolayers on Scribed Silicon**, ***L. Yang***, *Y.-Y. Lua, G. Jiang, M.R. Linford,* Brigham Young University

While chemomechanical modification of silicon with a variety of reagents is now well established, a significant amount of physical characterization remains to be performed on these new monolayers to understand their structures. Time-of-Flight Secondary Ion Mass (ToF-SIMS) was performed on monolayers on scribed silicon derived from 1-alkenes, 1-alkynes, 1-holoalkanes, aldehydes and acid chlorides. In order to best analyze the vast quantity of data that is produced by SIMS a chemometrics analysis was performed. Principle component analysis (PCA) proved to be a powerful tool for data compression and information extraction. Nine different PCA analyses were performed, including analyses of i) negative, ii) positive, and iii) combination of the negative and positive spectra, using i) normalized data, ii) normalized and mean-centered data, and iii) normalized and standardized data. If only normalization is performed the first PC loses most of its information content, as it mostly relates to the distance between the spectra (plotted as single points in a hyperspace) and the origin. If both normalization and standardization are performed it is difficult to extract information from the data because too much noise is given equal importance with the data. The positive and negative ion spectra contain complementary information. PCA of negative ion spectra gave a good separation of the monolayers according to the types of adsorbates used in monolayer preparation. PCA of positive ion spectra primarily separated the monolayers according to the number of carbons in their precursor. PCA of the combined positive and negative ion spectra is similar to that of negative spectra. Loadings plots showed the variables that best account for the variability in the data. PCA also indicates the presence of a few outliers in a large set of data, which further shows the usefulness of this method for demonstrating and confirming surface quality. The results of this study are an excellent confirmation of monolayer formation on scribed silicon from a series of different precursor molecules.

Applied Surface Science
Room 210A - Session AS+BI-WeA

Biological Applications of Surface Analysis

Moderator: A. Belu, Medtronic

2:00pm **AS+BI-WeA1 G-SIMS-MS: Towards Molecular Structure at Surfaces***, **I. Gilmore**, F. Green, M. Seah,* National Physical Laboratory, UK

SSIMS is a powerful technique for the analysis of complex surfaces. However, many view SSIMS as an excellent research tool but unreliable as an analytical method. This is changing. Modern instruments have superb repeatability and reliability. In the VAMAS 2002 SSIMS inter-laboratory study, the average repeatability of 27 instruments was already 2%. Accessibility to SSIMS measurements is increasing rapidly. However, the complexity of mass spectra makes identification and quantification far from straightforward, even for the experts! This is a major barrier to the wider take-up of SSIMS, especially in new fields. One way around this problem is G-SIMS. G-SIMS or gentle SIMS is a library independent method providing a straightforward way to simplify SSIMS spectra@footnote 1 @@footnote 2 @@footnote 3 @. SSIMS spectra are composed of parent fragment ions amongst a large number of high intensity degradation products. In G-SIMS, this fragmentation may be quantified in terms of the partition functions of the fragments emitted from a surface plasma with effective temperature, T@sub p@. By extrapolation of the data to low T@sub p@, the intensity of the degradation products rapidly reduces, revealing the parent fragments. The latter peaks are directly characteristic of the material without rearrangement and can enable direct interpretation and identification. This is fine for smaller molecules but, within the plethora of possible larger molecules for which a total mass is insufficient to provide adequate characterisation, an extension of G-SIMS has exciting prospects to elucidate the required structure. Here we use, G-SIMS-MS, to explore the re-building of parent molecules using the fragmentation pathways that are mapped out as T@sub p@ is varied. @FootnoteText@ @footnote 1@ I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000) 465. @footnote 2@ I S Gilmore and M P Seah, Appl. Surf. Sci., 187 (2002) 89. @footnote 3@ I S Gilmore and M P Seah, Appl. Surf. Sci., 203-204 (2003) 551.

2:20pm **AS+BI-WeA2 Functional Molecular Surfaces for Healthcare - Characterisation, Analysis and Understanding***, **M.C. Davies**, S.J.B. Tender,* University of Nottingham, UK*; P.M. Williams,* University of Nottingham, UK, U.K.*; C.J. Roberts, S. Allen,* University of Nottingham, UK **INVITED**

The characterisation of the surface structure of both conventional and advanced biomedical systems can be an important step in understanding the performance and optimising the function of such healthcare devices. A number of advanced biophysical analytical techniques have emerged for the study of pharmaceutical and biomedical systems. In this talk, we shall explore the role of these analytical tools as complimentary techniques, in the study of surface structure and function of advanced polymeric materials. The value and limitations of visualisation of surface topography and morphology of polymeric devices will be discussed and will include the condensation of polymeric constructs for gene therapy to the single molecule imaging of micro-patterned proteins on nanoengineered tissue-engineering substracts. The role of the force microscope in determining interparticulate and inter-molecular forces in order to explore its potential for the study of biomolecular interactions at polymer interfaces through to the macromolecular stimuli response hydrogels will be reviewed. The potential of the biophysical methodology of high-resolution imaging and force spectroscopy to aid research in biorecognition, development of gene delivery systems and understanding interparticulate and molecular forces, will be highlighted. The ability to identify the chemical structure of the molecules laterally across of a surface for both model and complex multiplayer patterned macromolecular assemblies shows promise but faces major challenges to low surface density ligands and high throughput array systems. The need for new approaches for handling large data sets of surface information and their relationship to surface functionality remains a significant challenge. The talk will aim to provide an objective assessment of current status, future challenges and opportunities.

3:00pm **AS+BI-WeA4 Model Calculations for the Quantification of XPS-Results; Application to Self Assembled Monolayers on Gold***, **C. Van der Marel**, J.H.M. Snijders, H.R. Stapert,* Philips Research, The Netherlands

XPS-analysis is widely applied for the characterization of surfaces and multilayers of thin films. In order to obtain quantitative results, the XPS peak areas generally are divided by appropriate sensitivity factors and normalized to 100 at% to obtain the apparent concentrations. Within the model developed by us, the sample is assumed to consist of a substrate on top of which a number of homogeneous layers are present. Starting from the apparent concentrations, the model calculation provides the thickness, the number of sulphur atoms per surface area and the composition of all layers. The proposed method requires only one measurement at one measuring angle to obtain these results. The method has been verified for a large series of self assembled monolayers made of mercaptoalkyl-polyethylene glycol compounds with various chain lengths on gold-plated Si. The influence of deposition time upon the obtained SAM-layers was examined; also SAM-layers deposited from mixtures of molecules with different chain length were investigated. RBS analysis was applied to determine in an independent way the amount of sulphur at the gold surface (expressed in number of Sulphur atoms per unit area); the RBS results correlated well with the XPS data. Also XPS-results obtained from mixtures of mercaptodeca-triethylene glycol and biotinylated thiols were analyzed in this way. The method resembles the calculation method proposed recently by Petrovykh et al@footnote 1@. Yet, in the latter method the analysis is restricted to only one layer on top of a substrate. Moreover, ion-etching is required to obtain a reference signal of the gold substrate; the consequence is, that elastic scattering of Au4f-electrons in the top layer is partly neglected in Ref.@footnote 1@. @FootnoteText@ @footnote 1@ D. Y. Petrovykh, H. Kimura-Suda, M.J. Tarlov and L.J. Whitman, Langmuir 20 (2004) 429.

3:20pm **AS+BI-WeA5 Surface Analysis by Friction Force Microscopy***, **G.J. Leggett**,* University of Sheffield, UK*; N.J. Brewer,* Dundee University, UK*; K.S.L. Chong,* University of Sheffield, UK

The characterisation of surface chemical structure on the nanometre scale still presewnts significant challenges. Friction force microscopy (FFM) is a widely accessible technique typically provided as standard on commercial atomic force microscoopes. It is capable of providing significant insights into variations in surface chemical composition and molecular organisation. The sensitivity of FFM to changes in molecular organisation will be illustrated with data from studies of self-assembled monolayers (SAMs) on Au and Ag. It will be shown that unexpected packing density differences, revealed by FFM, correctly predict the variation in the photo-oxidation kinetics of these materials. FFM suggests that while SAMs of methyl temrinated adsorbates on Ag are more closely packed on than they are on Au, the reverse is the case for monolayers of carboxylic acid terminated thiols. Methyl terminated SAMs on Ag oxidise more slowly than similar monolayers on Au, while the reverse is true for carboxylic acid terminated SAMs, reflecting the strong influence of molecular packing on photo-oxidation kinetics. The kinetics of SAM photo-oxidation have also been studied and quantified by FFM. Samples of carboxylic acid terminated thiols were exposed to UV light for varying periods of time and then immersed in solutions of methyl terminated thiols. Oxidised adsorbates were replaced by solution-phase thiols. For macroscopic samples, the variation in the coefficient of friction determined by FFM as a function of SAM photo-oxidation correlates closely with the variation in the contact angle (ie, as oxidation proceeds the SAMs become increasingly hydrophobic, and exhibit an increasingly small coefficient of friction). Similar types of analysis may be used to quantify rates of reactions in photopatterned materials SAMs. For materials with structures as small as a few tens of nm, fabricated by scanning near-field optical lithography, FFM enables the monitoring of chemical reactivity.

3:40pm **AS+BI-WeA6 Synthesis, Characterization and Modeling of Tethered Poly (N-isopropylacrylamide)***, **S. Mendez**, G.P. Lopez,* The University of New Mexico*; H. Yim, M.S. Kent, J.G. Curro,* Sandia National Laboratories*; J.D. McCoy,* New Mexico Tech

Tethered polymers are widely used to control surface properties such as adhesion and wettability. By making thin films out of polymers that are thermo-responsive, we can modulate surface properties with changes in temperature. Specifically, we use poly(N-isopropylacrylamide) (PNIPAM) since this exhibits lower critical solution temperature (LCST) behavior near 32 degrees Celsius in water. At temperatures below the LCST, the polymer is hydrated and swollen, whereas above the LCST, the polymer collapses, and when tethered, the surface becomes more hydrophobic. We report a method of growing PNIPAM from mixed self-assembled monoloyers (SAMs) using atom transfer radical polymerization. The use of two-component SAMs with varying composition permits for the control of polymer surface coverage, and the molecular weight can be controlled by the polymerization time. We have used both surface plasmon resonance and neutron reflectivity techniques to make direct measurements of the polymer brush structure at temperatures above and below the solution LCST. The effects of polymer surface coverage and molecular weight on the polymer structure were investigated. To model the temperature-induced structural changes of these brushes, we employed self-consistent field (SCF) theory using as input the chi parameter extracted from the experimental polymer solution phase diagram. The brush structure as predicted by SCF theory is in qualitative agreement with experimental data.

4:00pm **AS+BI-WeA7 Reversible Control of Free Energy and Topography of Nanostructured Surfaces***, **Q. Fu**, G.V. Rama Rao, S.B. Basame, D.J. Keller, K. Artyushkova, J.E. Fulghum, G.P. Lopez,* The University of New Mexico

We describe a facile method for the formation of dynamic nanostructured surfaces based on the modification of porous anodic aluminum oxide with poly(N-isopropyl acrylamide) (PNIPAAm) via surface-initiated atom transfer radical polymerization. These hybrid membranes were characteriazed by FTIR, TGA, SEM. The dynamic structure of these surfaces was investigated by atomic force microscopy (AFM), which showed dramatic changes in the surface nanostructure above and below the aqueous lower critical solution temperature of PNIPAAm. These changes in surface structure are correlated with changes in the macroscopic wettability of the surfaces, which was probed by water contact angle measurements. Principal component analysis was used to develop a quantitative correlation between AFM image intensity histograms and macroscopic wettability. Such correlations and dynamic nanostructured surfaces may have a variety of uses.

4:20pm **AS+BI-WeA8 Characterization of Bound Nucleotides using XPS and ATR-FTIR***, **D.B. Barbash**, J.E. Fulghum, G.P. Lopez, Y. Wu,* The University of New Mexico

In this work we utilize XPS and ATR-FTIR to probe the attachment of nucleotides to self-assembled monolayers. The attachment of DNA onto functional surfaces is utilized in applications ranging from DNA microarray technology to molecular wires. We are utilizing nucleotides as model systems in the development of surface-specific methods for the analysis of bound DNA. The nucleotides or DNA are covalently bound to self-assembled monolayers on glass or gold substrates using a diazotization-based method we recently developed (Dolan, P.L. et al. Nucleic Acids Research 2001, 29, 21e107). Three of the four nucleotides can be attached using this method, and we report unique spectral signatures for the nucleotide bases adenine (dATP), cytosine (dCTP), and guanine (dGTP) based on ATR-FTIR and XPS analyses. Based on these spectral signatures, results of competitive binding experiments will be discussed. XPS is also utilized to characterize the attachment steps and estimate surface coverage. ARXPS results of bound nucleotides will be discussed.

Manufacturing Science and Technology
Room 303B - Session MS+AS-WeA

Non-Destructive Analysis and Metrology for Advanced Manufacturing

Moderator: A. Testoni, Varian Semiconductor Equipment

2:00pm **MS+AS-WeA1 Advances in X-ray Reflectivity (XRR) and X-ray Fluorescence (XRF) Measurements Provide Unique Advantages for Barrier and Metal Layer Measurements of 65 nm Node Devices***, J.S. Spear,* Technos International*; H. Murakami, **S. Terada**,* Technos Company Limited, Japan

We have developed a thin-film metrology tool that fulfills the metrology requirements for the production of 65nm node technology and beyond. This tool combines X-ray Reflectivity (XRR) and X-ray Fluorescence (XRF) measurements to provide accurate, high throughput, measurements. Improvements in both the XRR and XRF configurations were made to allow high throughput measurements on films as thin as 0.5 nm. One of the challenges for the 65nm node is measuring the Cu metal layers and their accompanying barrier layers. The difficulty in measuring these layers is increased since the barrier is often a bi-layer composed of both TaN and Ta. This paper describes how a combined XRR XRF tool can be used to accurately measure these individual layers with optimum throughput.

2:20pm **MS+AS-WeA2 Non-Destructive Ultra-Thin Film (0-100A) Analysis in the Lab and the Fab.***, **C.R. Brundle**,* C. R. Brundle and Associates **INVITED**

Whether for characterization or failure analysis work in the support laboratory, or for rapid quality control/metrology in a wafer processing fab, the need for analytical techniques capable of determining thickness, composition, and composition as a function of depth (including differences at interfaces) is increasing as the variety of film material used in processing expands, and as films and stacks get thinner. The current materials roster, and the stringency of analytical requirements are briefly reviewed, then four non-destructive techniques being deployed in lab and fab situations are discussed and their capabilities compared for these two different environments. They are X-Ray Fluorescence, XRF; X-Ray Reflectivity, XRR; X-Ray Photoelectron Spectroscopy, (XPS and angle resolved XPS); and Low Energy X-Ray Emission spectroscopy, LEXES.

3:00pm **MS+AS-WeA4 Crystalline Structure and Stress Characterization in Thin Films by Means of Optical Spectroscopy***, **G. Conti**, Y. Uritsky,* Applied Materials, Inc.

Nondestructive characterization techniques are crucially important in developing new materials. Raman Spectroscopy is a powerful and versatile tool. Its capabilities range from structural identification and conformation of molecules, to identification of crystalline structure of materials. This power and versatility has led to its progressively more extensive applications to semiconductor industry as an analytical tool. In this paper we present some applications of Raman analysis to the characterization of thin films. The present challenge in thin films characterization is on one hand the determination of the film composition and/or crystalline phase; on the other the stress to which the film is subjected as it is deposited under different temperatures, chemical conditions of depositions, and substrates. In the first part, we report on the Raman characterization of silicides films generated on a Si surface. In particular we determine the stoichiometric composition of the silicides, their crystalline phase and their thickness. In the second part, we determine the stress of Si deposited on SiGe. The main advantage of Raman versus conventional X-ray diffraction is the ability to measure strain in thin layers (from 5 nm and above). We show here that Raman is the ideal method for characterizing strained cap Si layers with critical thickness in the range of 100-200 Å., and for characterizing stresses in quantum wires, quantum dots and other hetero-structures, which are becoming more and more important for fabricating devices with enhanced performance.

3:20pm **MS+AS-WeA5 Optical Properties (IR to VUV) and Birefringence of Graphite-like Amorphous Carbon***, **S. Zollner**, R. Liu, R.B. Gregory, W. Qin, J. Kulik, N.V. Edwards, K. Junker,* Motorola*; T.E. Tiwald,* J.A. Woollam Co.

Amorphous carbon films of 50 nm thickness, low surface roughness, and low densities (1.5-1.7 g/cm@super 3@) were deposited on Si using plasma-enhanced chemical vapor deposition (PECVD) between 300 and 550°C. With increasing deposition temperature, the hydrogen content (determined with elastic recoil detection) is reduced from 35% to 15%. For films grown at lower temperatures, ellipsometry data (0.7 to 9.5 eV photon-energy range, taken at 35-75° angle of incidence on a rotating-analyzer ellipsometer with a computer-controlled Berek waveplate) can be fitted very well by a single optically isotropic layer with low visible absorption (@epsilon@@sub 2@1 Torr), the ion energy is expected to be very low, which leads to dominant sp@super 2@ character of our films@footnote 1@ (verified by electron energy loss spectrometry) and low density (

3:40pm **MS+AS-WeA6 Metrology for Advanced Manufacturing***, **M.I. Current**,* Frontier Semiconductor **INVITED**

Metrology for process controls for manufacturing of advanced semiconductor devices faces an unprecedented number of challenges, well beyond the continued scaling to smaller transistors and denser functional arrays. Some common themes are the sharp increase in the introduction of new materials, new materials combination and interfaces and new device structures. This review will consider the metrology challenges and some new methods in four areas: (1) ultra-shallow doped junctions, including dopant activation and leakage currents, (2) stress and adhesion characteristics of metal/dielectric interfaces for gate and interconnect stacks, (3) local strain characterization of isolation structures, gates and channels as well as wafer-scale, strained materials systems and (4) bonding and layer transfer methods for integration of heterogeneous materials and devices such as, multi-level SOI wafers for logic, memory and photonic devices, 3-D packaging of functionally diverse devices and integration of MEMS/photonic structures with CMOS devices.

4:20pm **MS+AS-WeA8 Total Analysis of the Gases in Semiconductor Manufacturing Process: Use of Ion Attachment Mass Spectrometry***, **M. Nakamura**, Y. Taneda, Y. Hirano, Y. Shiokawa,* ANELVA Technix Corporation, Japan*; M. Takayanagi, M. Nakata,* Tokyo University of Agriculture and Technology, Japan

Ion attachment mass spectrometry (IAMS)@footnote 1@ is a powerful tool to monitor semiconductor manufacturing process@footnote 2-3@ by analyzing the molecules in the gas because with IAMS fragment-free mass spectra can be obtained; i.e. only quasi-molecular ions without being suffered by dissociation are observed. The fragment-free detection is impossible with other ionization techniques such as the electron ionization. There are two-type equipments of IAMS; one for the process at the pressure from 100 Pa to atmospheric pressure, and the other for the process at several Pa. We analyzed the process for manufacturing semiconductor by measuring mass spectra of gases in the reaction chamber and of the exhaust gas simultaneously with these equipments. Very high frequency capacitively coupled plasma (VHF-CCP) (60 MHz, 1000 W) was produced in the reaction chamber by providing 2 Pa of Ar/c-C@sub 4@F@sub 8@/O@sub 2@ (100, 2, and 6 sccm, respectively). The equipment for gases at several Pa was installed on the sidewall of the reaction chamber with a connection pipe of 100-mm length. At the same time the exhaust gas from the reaction chamber was analyzed after the rough pump with the other IAMS equipment. Polymerized compounds such as carbonyl fluoloride (C@sub 4@OF@sub 8@, C@sub 5@OF@sub 10@, and so on) and other compounds were found not only in the exhaust gas@footnote 2@ but also in the reaction chamber. The kinds of compounds in the exhaust gas are less than those at the reaction chamber, suggesting the dissociation and the polymerization at the pumping line. We present in our talk about c-C@sub 4@F@sub 8@ plasma in other conditions, SiH@sub 4@ plasma, and other processes to show the applicability of IAMS. The authors are grateful to Dr. H. Ito et al. of ASET for their support to the experiments. @FootnoteText@ 1 T. Fujii, Mass Spectrom. Rev. 19, 111 (2000). 2 M. Nakamura et al., J. Vac. Sci. Technol. A 19, 1105(2001). 3 Y. Shiokawa et al., AVS Int. Sympo., PS-ThA1 (2003).

4:40pm **MS+AS-WeA9 Optimizing and Managing Calibration Gas Inventories to Address Accuracy, Analysis Shelf Life and the Cost of Ownership**, ***P. Somssich,*** Osram Sylvania, Inc.

Today's analytical laboratories must meet ever-stricter quality controls and tracking requirements to maintain accreditation. Maintaining the usability of certified gas standards can be both time-consuming and costly. An ACCESS-based database was developed at Osram Sylvania Inc. to serve both cost management needs and the scientific requirements. The essentials of such a database required addressing critical issues: e.g., the shelf life of the certification, the traceability and cost of ownership. Almost 28 certified gas mixtures have since been recertified with initial fill and analysis dates going back 16 years. While some older mixtures were initially thought to be no longer useable, actual analysis results indicated that in most cases the vendor stated shelf life was far too short. However, there were a few dramatic exceptions. In addition to the costs associated with maintaining the certification, significant costs can occur by way of cylinder rentals, i.e., long term rental. This data is currently being evaluated to minimize the cost of ownership of the inventory, which includes 140 mixtures. The importance of good and accurate (or even very accurate) gas calibration standards has recently been highlighted by the use of EPA protocol gases associated with continuous emission monitors (CEMs). Since the Clean Air Act of 1990 makes the use of such monitors necessary, proper calibration standards and procedures can contribute to a sizeable financial windfall, while poor calibration can result in possible stiff penalties. Applications from lamp manufacturing will also be discussed showing a significant quality and financial benefit when lighting products are filled accurately resulting in optimal light output and performance as well as energy savings.

Applied Surface Science
Room 210A - Session AS-ThM

High-k Dielectrics

Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:20am **AS-ThM1 Physical and Chemical Characterization of MOCVD Zirconia Films Deposited on Hydrogen-Terminated and Native Oxide Si Surfaces***, **B.R. Rogers**,* Vanderbilt Universirty*; Z. Song, R.D. Geil, R.A. Weller,* Vanderbilt University*; M.O. Bloomfield, T.S. Cale,* Rensselaer Polytechnic Institute

Successful replacement of silicon dioxide-based MOSFET gate dielectrics by a high-permittivity (high-k) dielectric is a critical step in the continued drive to build the smaller, faster, lower-power, more-integrated circuits that society is demanding. Our group has been studying zirconia films deposited via MOCVD on hydrogen terminated silicon and silicon native oxide surfaces. Process pressures on the order of 10@super -5@ torr were used along with substrate temperatures between 300 and 450 @degree@C. Films were characterized using AFM, TEM, AES, spectroscopic ellipsometry, time-of -flight medium energy backscattering, and XRD. Results show that films deposited on hydrogen-terminated silicon are rougher, and have a mainly tetragonal microstructure. In contrast, films deposited onto silicon native oxide are much smoother and have a mixture of tetragonal and monoclinic microstructure, the ratio of the two microstructures depended on the deposition temperature. In addition, grain sizes in films of similar thickness also depended on the surface on which the films were deposited. In situ spectroscopic ellipsometry analyses show that depositions on hydrogen-terminated silicon begin with and induction period (where no deposition occurs) followed by a linear growth. Depositions on silicon native oxide have no induction period, initiating immediately into linear growth. Results from additional analysis techniques, along with simulation of the nucleation/growth process provide insight into the reason why films of different properties are deposited onto the two surfaces. This work is supported by the National Science Foundation grant # CTS-0092792.

8:40am **AS-ThM2 Challenges for the Characterization and Integration of High-k Dielectrics***, **R.M. Wallace**,* University of Texas at Dallas **INVITED**

The integration of advanced gate dielectric materials into CMOS technology presents several significant challenges.@footnote 1,2@ Moreover, the introduction of these materials is expected to occur at an unprecedented pace to meet industry technology forecasts. Although recent research has focused on the search for a material that yields a suitable (higher) dielectric constant than the industry benchmark SiO@sub 2@, a more important problem is the actual integration of any new dielectric material in existing CMOS flows in a cost-effective manner. These integration issues include etching, constituent stability, control of phase segregation and crystallization, dopant penetration, as well as gate electrode compatibility, which influence the resultant electrical properties. The study of these issues require substantial efforts in physical and electrical characterization. This talk will examine several of these integration issues in view of recent characterization studies and the associated challenges that must be addressed for successful high-k gate dielectric integration. This work is supported by the Texas Advanced Technology Program. @FootnoteText@@footnote 1@G.D.Wilk, R.M.Wallace and J.M.Anthony, J. Appl. Phys., 89, 5243 (2001). @footnote 2@R.M.Wallace and G.D.Wilk, Crit. Rev. in Sol. State Mat. Sci, 28, 231 (2003).

9:20am **AS-ThM4 Engineering the Properties of Hf-based Gate Dielectrics: Role of Initial Surface Preparation and Post Deposition Annealing***, R. Puthenkovilakam, **Y.-S. Lin**, J.P. Chang,* University of California, Los Angeles

Alternative gate dielectrics such as HfO@sub 2@ or HfO@sub x@N@sub y@ are required in the future generations of MOSFET devices to enable their rapid down-scaling. However, the material and electrical properties of these materials are not fully understood or optimized. In this work, we investigate the material and electrical properties of ultra thin HfO@sub 2@ and HfO@sub x@N@sub y@ films on Si, deposited by an atomic layer controlled deposition process involving alternate pulses of Hf-t-butoxide precursor and oxygen (or NH@sub 3@). Post deposition annealing was performed in-situ in O@sub 2@, N@sub 2@, N@sub 2@O, NH@sub 3@ and ex-situ in H@sub 2@/D@sub 2@. X-ray photoelectron spectroscopy (XPS) measurements indicated the formation of interfacial layer and its structural changes upon post-deposition will be addressed. Extended x-ray absorption fine structure (EXAFS) measurements indicated that the short-range order in the as-deposited HfO@sub 2@ films resembled to that of the monoclinic phase HfO@sub 2@ and showed signs of crystallization upon annealing, while N incorporation seems to change the short-range order in the films and increase the crystallization temperature. Capacitance-voltage (C-V) measurements were performed on MOS devices to extract the dielectric constants (k), flat band voltage shifts, and interface state density. The as-deposited samples yielded k-values from 15-23 and their leakage currents were significantly less than that of SiO@sub 2@ films at the same equivalent oxide thickness (EOT). Temperature dependent current-voltage (I-V) measurements were performed to elucidate the conduction mechanisms in these ultra thin films. Substrate injection resulted in Schottky-like current transport while the gate injection showed a tunneling mechanism. The effect post-deposition annealing on the electrical performance will also be addressed in this talk in detail.

9:40am **AS-ThM5 Applications of ARXPS to Semiconductor Fabrication and Characterization***, **P. Mack**, M. Shakespeare, A. Wright, R.G. White,* Thermo Electron Corporation, UK

In modern semiconductor fabrication, two trends are clear. Layers are becoming thinner and the materials are becoming chemically more complex. For these reasons, XPS is becoming increasingly important as a characterisation tool. It is well known that XPS provides chemical state information from the near surface region and commercial tools exist to handle wafers of up to 300 mm. Now that the thickness many of the layers used in semiconductor technology are less than the escape depth of the photoelectrons, the technique can be used to characterise the layers and their interface with the substrate. If angular resolution is combined with the XPS technique (angle resolved XPS or ARXPS) it becomes possible to measure the thickness of layers, and the distribution of the materials and chemical states within the layer non-destructively. For example, not only can ARXPS measure the thickness of an oxynitride layer but it can also determine the way in which nitrogen is distributed through the layer. The nitrogen distribution affects both the electrical properties and the accuracy of dose measurements. In the case of high-k dielectrics, the nature and thickness of both the high-k layer and any intermediate silicon dioxide or silicate layer can be determined. The combined electrical properties of these layers determine the integrity of the dielectric stack. By using the technique of parallel ARXPS it becomes possible to make all of these measurements from intact 300 mm wafers. ARXPS can produce depth profiles without the need for sputtering. This means that ARXPS has the potential to be applied to shallow implants, such as arsenic in silicon. This has the advantage over SIMS profiles that it does not suffer from near-surface sensitivity artefacts. Examples of materials characterisation from a range of semiconductor thin films will be shown.

10:00am **AS-ThM6 ALD and MOCVD Growth of High K Dielectric Al and Hf Films Studied by Parallel Angle Resolved XPS (PARXPS)***, **R.K. Champaneria**,* Thermo Electron Corporation, UK, England*; P. Mack, J. Wolstenholme, R.G. White,* Thermo Electron Corporation, UK

XPS has been identified as being a suitable technique for the characterisation of surfaces and ultra thin layers encountered in semiconductor device fabrication. The extension of this technique to angle resolved XPS, ARXPS allows quantification of elemental and chemical state concentrations in the region of 5 to 10nm, a thickness that is well matched with the gate dielectric thickness currently used. By using maximum entropy calculations it is possible to generate non-destructive atomic concentration depth distribution plots from ARXPS data. These plots show the integrity of a film as well as the behaviour of interfacial layers. This paper looks at Al and Hf films grown by ALD and MOCVD processes. It shows differences in the state of the grown or deposited film as well as changes to the interfacial layer depending on how the film is grown and the thickness of the film. In addition, surface pre-treatment is also found to have a dramatic affect on the nature and role of the interfacial layer For Al and Hf multilayer films the integrity, thickness, preferential growth and the role of the interfacial layer are also investigated.

10:20am **AS-ThM7 Comparative Study of Metal Oxy-Nitride Films by Electron Spectroscopy***, P.M. Mrozek, **D.F.A. Allgeyer**, B.C. Carlson, K.B. Beaman, H.K. Krasinski,* Micron Technology, Inc.

X-ray photoelectron spectroscopy (XPS) was used extensively to provide information regarding the chemical composition and chemical states of the nitrogen in silicon, hafnium, and other oxy-nitride films grown on silicon or tungsten substrates. Different substrates were investigated in order to minimize differential charging effects. Nitride and ON-like states were identified in different films, and their depth distributions were found to vary from film to film. Nondestructive angle-resolved XPS analysis was applied to reconstruct elemental distributions in films and showed a nitridization depth of ~4nm for SiON and below 2nm for HfON. These results were compared with activation enthalpy for nitridization for different systems.

10:40am **AS-ThM8 Development of Reference Thin Films for Gate Oxide Thickness Determination and Ultra Shallow Junction Profiling*, D.W. Moon,*** KRISS, Korea **INVITED**

With the continued scaling down of CMOS devices beyond 50 nm, accurate and precise measurements of gate dielectric layer thickness and dopant profiles in ultra shallow junctions are no more simple and straightforward even with sophisticated techniques. In this presentation, the current status and remaining issues in analytical methodology for gate oxides and ultra shallow junctions are summarized and discussed. For accurate measurement of nm gate oxides thickness with sub atomic layer thickness precision, the thickness that each technique generates can be different and the difference should be understood in a complementary nature. Compared and discussed are the differences between high resolution transmission electron microscopy, grazing incidence X-ray reflectivity, medium energy ion scattering spectrometry, X-ray photoelectron spectroscopy, ellipsometry for accurate and precise determination of gate oxides down to sub nm thickness. For ultra shallow junction depth profiling, details of the sputtering processes in low energy secondary ion mass spectrometry are investigated regarding to the damage profiles and surface transient sputtering effect. Development of multiple delta layer reference thin films for ultra shallow junction profiling is reported on the growth and the application for sputtering rate calibration including the surface transient effect. Relevant activities of ISO TC 201 Surface Chemical Analysis and CCQM Surface and Micro/Nano Analysis WG and the present status and issues of reference thin films for gate oxide thickness determination and ultra shallow junction profiling will be briefly discussed.

11:20am **AS-ThM10 XPS and SIMS Analysis of HfSiON Films*, S. Miwa,*** *S. Kusanagi, Y. Murakami, H. Kobayashi,* Sony EMCS Corp., Japan

Nitrided Hafnium-silicate (HfSiON) is one of the promising materials for high-k gate dielectrics in advanced CMOS LSI. This material is so new that we have to investigate not only its electrical performance but also its chemical and physical properties. X-ray Photoelectron Spectroscopy (XPS) is the conventional technique for analyzing the chemical composition of thin films. We have found that XPS can also confirm the presence of phase separation in HfSiON films from the peak shift of the O1s signal. Secondary Ion Mass spectrometry (SIMS) is the most frequently used method to detect impurities in thin films and semiconductor substrates. In the case of high-k films grown by atomic-layer deposition or metal-organic chemical vapor deposition, it is necessary to use SIMS to determine whether H or C from precursor has been incorporated. SIMS can also be used N distribution in HfSiON films. However, it is difficult for conventional SIMS to observe the diffusion of Hf from HfSiON film to the Si substrate. Hf is moved from the film to the Si substrate by the probe ion beam, so we have employed backside-SIMS to observe Hf diffusion and obtain the precise Hf distribution near the HfSiON/Si interface.

11:40am **AS-ThM11 Nitridation of Hf Silicate Layers for Advanced CMOS Gate Oxides : A Core Level and Valence Band Study by Photoelectron Spectroscopy*, O. Renault,*** CEA-DRT-LETI, France*; N. Barrett, F. Calvat,* CEA-DSM-DRECAM, France*; Y. Le Tiec,* CEA-DRT-LETI, France*; P. Besson,* ST-Microelectronics, France*; F. Martin,* CEA-DRT-LETI, France

The nitridation of high-k materials is widely investigated for sub-65nm CMOS technology nodes@footnote 1@.In this contribution, we will present recent results of a core-level and valence band study by photoelectron spectroscopy, using both synchrotron and AlKa radiation, of nitrided Hf-silicate films for advanced gate oxides. Hf-silicate layers (3.5 nm-thick) were grown onto thin oxidized Si surfaces and then nitrided in an NH3 ambient. The valence band study at 80 eV photon energy reveals the introduction, upon nitridation, of localized N2p electronic states in the band gap of the silicate, thus confirming recent theoretical predictions@footnote 2@. The core-level analysis (Hf4f, N1s, Si2p) of as-grown, partially and totally etched silicate layers indicates that nitridation creates Hf-N bonds with a gradient from the surface to the interface depending on the nitridation temperature. Spectra recorded using synchrotron radiation with enhanced surface sensitivity and photon energy tunability will be presented and highlighted emphasizing the possibility to isolate the Si bonding states from the silicate layer itself. @FootnoteText@ @footnote 1@ M. Koike et al., extended abstracts, IEDM, 107 (2003).@footnote 2@ G. Shang, P. W. Peacock, J. Robertson, Appl. Phys. Lett. 84, 106 (2004).

Biomaterial Interfaces
Room 210D - Session BI+AS+SE-ThM

Surface Modification of Biomaterials

Moderator: D.G. Castner, University of Washington

8:20am **BI+AS+SE-ThM1 Strategies for the Biofunctionalization of Surfaces using Functional Polymer Layers*, J. Ruehe,*** University of Freiburg, Germany **INVITED**

The modification of surfaces with polymers for the promotion of cell outgrowth either in a dense layer or following a distinct pre-determined pattern is a challenging field of research with possible applications in the field of medical implants as well as for specific sensor devices. We present results from various studies in our group that range from the modification of bioimplant surfaces (e.g. glutar aldehyde treated porcine heart valves) with polymer monolayers in order to allow for a re-endothelialization of these devices to the arrangement of neuronal cells on a substrate by depositing synthetic and natural polymers on these chips in the form of a microarray. We will put a strong emphasis on synthetic approaches for establishing a strong, i.e. usually covalent interaction between the polymeric coating and the substrate in order to guarantee a sufficient long-term stability of the layer assemblies. These assemblies may be polymer monolayers as well as networks and we will also report on strategies for the incorporation of biological functions such as cell adhesion motifs or peptides. Finally, approaches for the laterally patterned deposition of these layers will be discussed.

9:00am **BI+AS+SE-ThM3 Interfacial Biomaterials: Guiding Biology on Synthetic Surfaces***, E.B. Walsh, X. Huang,* Duke University*; M.W. Grinstaff,* Boston University*; **D.J. Kenan,*** Duke University Medical Center **INVITED**

Interfacial biomaterials represent a novel coating technology capable of directing biological processes at the interface between a biologic and a synthetic surface. The approach relies on screening combinatorial libraries to identify unique peptides that adhere to a synthetic target such as a plastic or metal, or to a biological target such as a protein or cell. Next, two or more adhesion peptides are synthetically coupled to create an interfacial biomaterial that mediates the interaction of the protein or cell with the synthetic material. Other interfacial biomaterials may be created by coupling known signaling molecules to peptides that bind synthetic materials. Mixtures of interfacial biomaterials may be applied to a surface to achieve a particular desired biological outcome, such as adhesion of a given cell type to the surface, followed by induction of one or more signal transduction pathways. These interfacial biomaterials are amenable to numerous coating and patterning techniques suggesting their use for diverse applications ranging from biomedical device coatings to anti-infectives to tissue engineering.

9:40am **BI+AS+SE-ThM5 Antibacterial Surfaces of Covalently Immobilized Dendrimers***, D. Weber, N.R. Choudhury,* University of South Australia*; **H.J. Griesser,*** University of South Australia, Australia

The need to limit bacterial adhesion to surfaces of biomedical implants, contact lenses, and other devices has prompted considerable recent research into antibacterial compounds and coatings. To ensure long-term efficacy and eliminate concerns about potential adverse biological effects on sensitive organs remote from the implant site, release strategies seem less suitable, and the covalent surface immobilization of antibacterial compounds is the approach of choice in our work. However, the question then becomes whether a covalently immobilized antibacterial is still biologically active, and can maintain activity over extended service life spans. In this study we have principally explored the surface immobilization of dendrimers, which have previously been shown to be antibacterially active in solution (eg CZ Chen and SL Cooper, Biomaterials 23 3359 2002). Another approach involves extracts of some Australian plant species, but their chemical characterization and synthesis is less developed. We have immobilized amine-terminated dendrimers onto aldehyde plasma polymer interlayers via reductive amination and characterized the coatings by XPS, ToF-SIMS, and AFM. Using various plasma conditions the surface density of aldehyde groups can be varied. The surface density of immobilized dendrimers is determined from XPS elemental ratios, using the dendrimer-specific N signal. Following surface immobilization, the remaining amine groups are quaternized in order to produce a cationic surface. The distinct signal arising from quaternary N in the XPS N 1s spectrum enables assessment of this reaction. The plasma approach also enables us to apply this coating strategy onto a wide variety of substrates both polymeric and inorganic (ceramic and metallic).

10:00am **BI+AS+SE-ThM6 Biomimetic Vascular Engineering: Exploiting Concepts from Nature to Create New Biomaterial Interfaces***, **R.E. Marchant**,* Case Western Reserve University **INVITED**

The abundance of complex supramolecular structures in Nature provides lessons in structural hierarchy and functional efficiency that are being explored and exploited in the development of novel biomimetic strategies for creating new biomaterial interfaces for biomedical applications. Mimicking and adapting structural concepts from Nature to create tissue compatible interfaces for biomaterials that incorporate molecular recognition and self-assembly will be the central theme of this presentation. We have developed a biomaterial architecture using "surfactant polymers" that undergo surface and self-induced assembly on hydrophobic surfaces. Our biomimetic designs benefit from understanding the structural and functional properties of the corresponding system in Nature. One example is the external region of a cell membrane, known as the glycocalyx, which is dominated by a complex milieu of glycosylated molecules. The glycosylated molecules direct specific interactions such as cell-cell recognition, and provide an important physical basis for maximizing steric repulsion that prevents undesirable non-specific cell and molecular adhesions. Conversely, understanding the nature of a cellâ?Ts adhesive interactions with the extracellular matrix facilitates design of biomimetic materials with cell adhesion properties. Using these biomimetic concepts, we have designed and studied oligosaccharide and peptide surfactant polymers that provide suppression of non-specific protein interactions and facilitate well-controlled interactions with endothelial cells.

10:40am **BI+AS+SE-ThM8 Stability of Polypeptide Multilayers as Studied by in situ Ellipsometry: Effects of Drying and Post-Buildup Changes in Temperature and pH***, T.J. Halthur,* YKI AB, Institute for Surface Chemistry, Sweden*; P. Claesson,* KTH, Royal Institute of Technology, Sweden*; **U. Elofsson**,* YKI AB, Institute for Surface Chemistry, Sweden

Polyelectrolyte Multilayers (PEM) of poly(L-glutamic acid) (PGA) and poly(L-lysine) (PLL) with a initial layer of polyethyleneimine (PEI) were built on silica and titanium surfaces using the Layer-by-Layer (LbL) technique. The stability of the film during drying/rewetting, temperature cycles and pH shifts was studied in situ by means of ellipsometry. The filmthickness was found to decrease significantly (approximately 70%) upon drying, but the original film-thickness was regained upon rewetting and the buildup could be continued. The dry thickness was found to be extremely sensitive to ambient humidity, needing several hours to equilibrate. Changes in temperature and pH was also found to influence the multilayer thickness, leading to swelling and de-swelling of as much as 8% and 10-20% respectively. The film does not necessarily regain its original thickness as the pH is shifted back, but instead shows clear signs of hysteresis.

11:00am **BI+AS+SE-ThM9 PCA of TOF-SIMS Spectra from p(AAm-co-EG/AAc) IPNS on Quartz***, **D.J. Graham**,* University of Washington*; G.M. Harbers, K.E. Healy,* University of California, Berkeley*; D.G. Castner,* University of Washington

PCA of TOF-SIMS has been carried out on many well defined model surfaces in structured experiments. These studies have shown the utility of PCA in extracting information from TOF-SIMS experiments from a wide variety of substrate surfaces. This work reports on the application of PCA to a more complex interpenetrating polymer network system. The goal of this project was to verify each step in the IPN synthesis procedure on a quartz substrate. This system presents a challenge to PCA due to the similarity of the polymers used in the IPN and the addition of a peptide chain. PCA of the entire data set (including all synthesis steps for the IPN) showed that PC1 was able to separate most samples. The PC1 loadings were dominated by the overall differences between the hydrocarbons on the bare quartz and the PEG related peak fragments after the addition of the IPN onto the quartz surface. This is likely due to the high PEG content of the IPN polymers. PCA comparing each successive synthesis step gave further insight into the success of the IPN chemistry. PCA was able to distinguish each surface modification up until the addition of the peptide precursor and peptide. The presence of the peptide was verified in subsequent experiments where it was shown that RGD-peptide modified p(AAm-co-EG/AAc) surfaces supported rat calvarial osteoblast adhesion, proliferation, and matrix mineralization. Consequently,surfaces without the RGD peptide or with a control RGE peptide did not support cell attachment. PCA also gave insight into the uniformity of the surface modifications by way of the scores plots. Increasing scatter was seen in the last few synthesis steps suggesting that a less uniform surface chemistry was achieved. The trends seen in the PCA of the TOF-SIMS data were consistent with those seen by XPS.

11:20am **BI+AS+SE-ThM10 Development of an Antimicrobial Polymer Surface Coating for the Prevention of Staphylococcal Infections***, **M. Anderle**, L. Pasquardini, L. Lunelli, R. Canteri, P. Villani, C. Pederzolli,* ITC-irst, Italy

The proliferation of pathogenic microorganisms on polymer surfaces is one of the most widespread causes of failure of biomedical devices such as catheters, medical implants, vascular graft and joint prostheses. The inhibition of pathogenesis and subsequent mechanisms of protection are possible by killing bacteria in the first steps of colonization. This work describes a polymeric surface coating with liposomes as method to provide a sustained delivery of antibiotics into the local micro-environment of the implant. In this study liposome formulations composed of Phosphatidylcholine (PC), Distearoyl-sn-Glycero-3-Phosphoethanolamine-N-MethoxyPolyethylene glycol (DSPE-PEG) and cholesterol are utilized. Liposomes, different in size, are attached to an amine activated substrate through the formation of covalent bonds with the distal end of the PEG (Polyethylene glycol) derivative molecules. Data on the surface coating using large unilamellar vesicles (LUV) and multilamellar vesicles (MLV) will be shown. The AFM analysis is performed to study the nanoscale structure of the coated surface while the fluorescence spectroscopy and microscopy are engaged to determine the immobilisation efficacy adding a fluorescent lipid (L-@alpha@-Phosphatidylethanolamine-N-lissamine rhodamine B sulfonyl) to the liposome composition. The MLV coating on polystyrene shows a more uniform distribution with a lipid concentration of about 2x10@super 15@ mol/cm@super 2@. Finally drug (rifampicin) release and bacterial colonisation rates with their correlation will be reported.

11:40am **BI+AS+SE-ThM11 Spectroscopic Characterization of Surface-Immobilized Antibacterial Furanone Coatings***, **S. Al-Bataineh**, H.J. Griesser,* University of South Australia, Australia*; M. Willcox,* University of New South Wales, Australia*; L.G. Britcher,* University of South Australia, Australia

The colonisation by bacteria of biomedical devices presents a serious concern for human implant surgery. In this study, we explore how bacterial colonisation can be prevented by the appropriate design and fabrication of antibacterial coatings, with a major focus on surface-immobilised furanone molecules. These compounds are produced naturally by the marine algae, Delisea pulchra and are used as defence agents to prevent fouling on their surface@footnote 1@. Several studies have shown that brominated furanones as well as synthetic analogues possess potent antimicrobial activity against bacteria@footnote 2@@super ,@@footnote 3@. The previously used azide protocol was adopted to prepare furanone coatings@footnote 4@. XPS and ToF-SIMS results showed successful surface modifications and furanone immobilisation. Detailed analysis of the C 1s and N 1s XPS spectra using constrained curve fitting showed that they are more complicated than anticipated from the theoretical reaction scheme. In addition, the presence of a Br@super-@ peak partially overlapped with a C-Br peak indicated that furanones are partially degraded on UV illumination. More surface characterisations are needed for full understanding of the chemical reactions that occurred. Seven furanone compounds used in this study were tested for their ability to inhibit biofilm formation and growth of two bacterial strains, Staphylococcus aureus (Saur19) and Pseudomonas aeruginosa (Paur6206). Initial results are promising; detailed investigation of the efficacy of the coatings is ongoing. Furthermore, none of the compounds used in this study showed any cytotoxicity potential at the tested concentrations. @FootnoteText@ @footnote 1@ de Nys R. et al., 1995, 4:259-71.@footnote 2@ Kjelleberg S. et al., Patent No. PCT/AU99/00284, 1999.@footnote 3@ Read R. et al. PCT international application PQ6812, 2001.@footnote 4@ Muir B. et al., Proc. 6th World Biomat. Congr., Hawaii, May 2000, p. 596.

Applied Surface Science
Room 210A - Session AS-ThA
Fuel Cell, Catalytic, and Nanomaterials Characterization

Moderator: B. Beard, Akzo Nobel Chemicals

2:20pm **AS-ThA2 Nanoscale Effects on Ion Conductance of Layer by Layer Structures of Gadolinia-doped Ceria and Zirconia***, **S.A. Azad**, A.A. El-Azab, L.S. Saraf, O.M. Marina, C.W. Wang, D.E. McCready, S.V. Shutthanandan, S.T. Thevuthasan,* Pacific Northwest National Laboratory

Development of electrolyte materials that possess high oxygen ion conductance at relatively low temperatures is essential to improve the performance of electrochemical devices. Ceria, doped with a divalent or trivalent cation, exhibits higher ion conductance compared with yttria-stabilized zirconia, the major component currently used in solid oxide fuel cells (SOFC). In this research, we have synthesized layer by layer structures of gadolinia doped ceria and zirconia in order to determine the nanoscale effects on the ion conductance of these films. Highly oriented multilayered nanostructures of gadolinia-doped ceria and zirconia were grown on sapphire substrates using molecular beam epitaxy and were characterized by in situ reflection high energy electron diffraction (RHEED) and ex situ x-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM) and Rutherford backscattering spectrometry (RBS). The oxygen ion conductance, measured by surface impedance spectroscopy at relatively low temperatures, was found to increase with increasing number of layers in these films. Theoretical calculations were also performed to understand the effects of space charge regions induced by the thermodynamic equilibrium and impurity segregation as well as the influence of the grain microstructures on the electric transport processes in solid oxide materials. The defect electrochemistry model developed in our study allows the extrinsic element (Gd) to transfer across the interfaces and space charge regions are created as a result, counterbalancing the purely blocking effect observed in polycrystalline structures of ceria or zirconia. The elastic interactions in ceria and zirconia lattice as well as the individual layer thickness largely influence the transfer of Gd across the interfaces.

2:40pm **AS-ThA3 Physical and Chemical Properties of Ce@sub1-x@Zr@subx@O@sub2@ Nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) Surfaces: Synchrotron-based Studies***, **X. Wang**, J.A. Rodriguez, G. Liu, J.C. Hanson, J. Hrbek,* Brookhaven National Laboratory*; C.H.F. Peden,* Pacific Northwest National Laboratory*; A. Iglesias-Juez, M. Fernández-García,* Instituto de Catálisis y Petroleoquímica, CSIC, Spain

The physical and chemical properties of Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces (x@<=@0.5) were investigated with synchrotron-based techniques (high-resolution photoemission, time-resolved X-ray diffraction and X-ray absorption near-edge spectroscopy). CeO@sub2@ and Ce@sub1-x@Zr@subx@O@sub2@ particles in sizes between 3 and 7 nm were synthesized using a novel microemulsion method. The results of XANES (O K-edge, Ce and Zr LIII-edges) indicate that the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces have very similar electronic properties. The lattice constant decreased with increasing Zr content, varying from 5.40Å in CeO@sub2@ to 5.27Å in Ce@sub0.5@Zr@sub0.5@O@sub2@. Within the fluorite structure, the Zr atoms exhibited structural perturbations that led to different types of Zr-O distances and non-equivalent O atoms in the Ce@sub1-x@Zr@subx@O@sub2@ compounds. The nanoparticles were more reactive towards H@sub2@ and SO@sub2@ than the (111) surfaces. The Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces did not reduce in hydrogen at 300°C. At temperatures above 250°C, the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles reacted with H@sub2@ and water evolved into gas phase. XANES showed the generation of Ce@super3+@ cations without reduction of Zr@super4+@. There was an expansion in the unit cell of the reduced nanoparticles probably as a consequence of a partial Ce@super4+@-->Ce@super3+@ transformation and the sorption of hydrogen into the material. S K-edge XANES spectra pointed to SO@sub4@ as the main product of the adsorption of SO@sub2@ on the Ce@sub1-x@Zr@subx@O@sub2@ nanoparticles and Ce@sub1-x@Zr@subx@O@sub2@(111) surfaces. Full dissociation of SO@sub2@ was seen on the nanoparticles but not on the (111) surfaces. The metal cations at corner and edge sites of the nanoparticles probably play a very important role in interactions with the H@sub2@ and SO@sub2@ molecules.

3:00pm **AS-ThA4 Physical and Chemical Properties of Iron and Iron-Oxide Nanoparticles @footnote 1@***, **D.R. Baer**, J.E. Amonette,* Pacific Northwest National Laboratory*; J. Antony,* University of Idaho*; J.C. Linehan, D.W. Matson,* Pacific Northwest National Laboratory*; J.T. Nurmi,* Oregon Health and Sciences University*; K.H. Pecher,* Pacific Northwest National Laboratory*; R.L. Penn,* University of Minnesota*; Y. Qiang,* University of Idaho*; P.G. Tratnyek,* Oregon Health and Sciences University

Iron particles in solution have interesting and potentially useful chemical properties, including an ability to reduce chlorinated hydrocarbons in geochemical environments. Reaction studies indicate that the dechlorination reaction pathway can be altered by the structure and chemistry of the nanoparticles. To understand some of these effects we are synthesizing, characterizing, and examining the properties of Fe nanoparticles using a variety of methods. We have synthesized particles in solution and by vapor deposition methods and obtained commercially available materials for detailed study. Methods of particle characterization include TEM, XAS, Mossbauer, XRD, and XPS. A variety of properties are being examined including stability, physical, chemical and electronic structure, magnetic properties and reactivity. Similarities and differences of particles formed in different ways will be discussed along with results relating to particle stability and the impact of particle preparation and processing on reactivity in solution. @FootnoteText@ @footnote 1@ This work is supported by the US Department of Energy Office of Science and parts of the work were performed in the Environmental Molecular Sciences Laboratory a national scientific user facility sponsored by the DoE's Office of Biological and Environmental Research.

3:20pm **AS-ThA5 High-Pressure X-Ray Photoelectron Spectroscopy for Catalysis Research and Environmental Science***, **H. Bluhm**, D.F. Ogletree,* Lawrence Berkeley National Lab*; G. Ketteler,* Lawrence Berkeley National Lab, Univ. of California*; M. Haevecker, A. Knop-Gericke, E. Kleimenov, D. Teschner,* Fritz Haber Inst. of the Max Planck Society, Germany*; E.L.D. Hebenstreit,* Lawrence Berkeley National Lab*; V.I. Bukhtiyarov,* Boreskov Inst. of Catalysis, Russia*; M.K. Gilles, T. Tyliszczak,* Lawrence Berkeley National Lab*; R. Schloegl,* Fritz Haber Inst. of the Max Planck Society, Germany*; M. Salmeron, D.K. Shuh,* Lawrence Berkeley National Lab

High-pressure X-ray photoelectron spectroscopy is a versatile method for the study of gas/solid and gas/liquid interfaces. Recently two synchrotron-based high-pressure XPS spectrometers have been developed, one located at the Molecular Environmental Science beamline at the Advanced Light Source in Berkeley, the other operating at BESSY in Berlin. We have used these high pressure XPS instruments to investigate problems in environmental science and heterogeneous catalysis. In this talk we will discuss the influence of the gas phase on the XPS spectra. Since the incident X-ray beam does not only irradiate the sample surface but also the gas phase in front of the sample, gas phase XPS peaks appear alongside the surface peaks at sufficiently high pressures. The gas phase signal can be used to probe the composition of the gas in the volume in front of the sample and get information about, e.g. the conversion and yield in heterogeneous catalytic reactions. An important group of materials in environmental science are minerals, which are often insulators and therefore charge when irradiated by X-rays. However, the sample surface is discharged due to the ionization of the gas phase by the incident X-rays. The amount of this effect depending on gas pressure and composition will be discussed. We will also consider the proper referencing of the binding energy, and the FWHM of the gas phase peaks depending on gas pressure and work function of the surfaces in the vicinity of the probed gas phase volume. @FootnoteText@ The Advanced Light Source and this work are supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and the Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at Lawrence Berkeley National Laboratory under Contract No. DE-AC03-76SF00098.

3:40pm **AS-ThA6 The Structure and Growth of Single- and Double-Walled Carbon Nanotubes***, **J.-M. Zuo**,* University of Illinois at Urbana-Champaign **INVITED**

Single- and double-walled carbon nanotubes have potential applications for future electronics and nanomachines. However, as-grown carbon nanotubes have a dispersion of structures, which differ in both diameter and chirality, and electric and mechanical properties. Characterization of these nanotubes has been a challenge. Recently, we developed a coherent electron diffraction/imaging technique by forming a nanometer-sized parallel beam of electrons that can be used to record diffraction patterns from individual nanotubes. Furthermore, the combination of coherence and high angular resolution allows the over-sampling of diffraction pattern and solution of phase problem by ab initio phase retrieval, thus, imaging of carbon nanotubes. Using this technique, we have investigated a large number of single- and double-walled carbon nanotubes. We found that neither zig-zag nor arm-chair tubes is preferred for growth. Double-walled carbon nanotubes are generally incommensurate and there is a peaked distribution of spacings between two tubes. The implication of these findings will be discussed based on the growth mechanism of carbon nanotubes. The technique of coherent electron nanodiffraction and diffractive imaging by the solution of the phase problem is general and applicable to other nanostructures. @FootnoteText@ *In collaboration with J. Tao, J. Bording, Boquan Li, M. Gao, L. Nagahara, R. Zhang, R. Twesten and I. Petrov.

4:20pm **AS-ThA8 Carbon Nanotubes and Mo@sub 2@C Reduced Pt Usage for Fuel Cells***, **T. Matsumoto**, T. Komatsu,* University of Tsukuba, Japan*; Y. Chiku,* Sekisui Chemical Co., LTD., Japan*; Y. Nagashima, T. Yamazaki, E. Yoo,* University of Tsukuba, Japan*; H. Shimizu, Y. Sato, Y. Takasawa,* Sekisui Chemical Co., LTD., Japan*; J. Nakamura,* University of Tsukuba, Japan

Pt has been considered to be an essential catalyst for the polymer electrolyte fuel cell (PEFC), and one of the difficulties in spreading fuel cells due to the high price, limited resource and no substitute of Pt. We successfully reduce Pt loads by using carbon nanotubes and Mo@sub 2@C. The PEFC with the 0.2 mg/cm@super 2@-Pt/CNT catalyst is fond to show higher cell voltage at 0-600 mA/cm@super 2@ than that of the PEFC with the 0.5 mg/cm@super 2@-Pt/CB catalyst. The PEFC with the only 0.06 mg/cm@super2@-Pt/CNT gives more than 60% of the cell voltage of the PEFC of the 0.5 mg/cm@super 2@-Pt/CB catalyst at 0-600 mA/cm@super 2@. Carbon nanotubes (CNTs) are better electrodes of Pt than carbon blacks (CBs) presumably due to the more triple-phase formation, better conductivity and more space for gas diffusion [J. Nakamura et al., Chem. Comm., 2004, 840 and Catal. Today, in press]. TEM images showed that 2-4 nm Pt nanoparticles are deposited on the CNT surfaces. The Pt nanoparticles from H@sub 2@PtCl@sub 6@ are well-dispersed, while those from K@sub 2@PtCl@sub 4@ are agglomerated due to an auto catalytic reaction. XPS spectra show Pt was fully reduced to be deposited as metallic Pt nanoparticles. The pretreatment of CNTs to remove amorphous carbon is also important, and a careful treatment is necessary for dissolution by HNO@sub 3@ not to form bundles. We also find that Mo@sub 2@C can be a substitute of Pt for PEFC. It is surprising that a PEFC with the Mo@sub 2@C/CNT catalyst in the anode exhibits 60% cell voltages of the current PEFC with the Pt/CB catalyst (0.5 mg/cm@super 2@). XPS and XRD showed that Mo was fully carburized to form Mo@sub 2@C nanoparticles.

4:40pm **AS-ThA9 Surface Characterization and Surface Science Needs in Support of Automotive Fuel Cells***, **F.T. Wagner**,* General Motors Fuel Cell Activities **INVITED**

Polymer electrolyte membrane fuel cells (PEMFC's) show promise as power sources for high-efficiency light-duty vehicles giving very low emissions. This talk reviews some of the critical interfacial phenomena that must be understood if this promise is to be fully realized. Examples will be given of cases where surface analytical techniques have provided useful insights. Additional cases will be discussed in which extension beyond the capabilities of current surface analytical techniques will be required if critical information is to be obtained. Fuel cells predate the internal combustion engine, but two developments since the 1980's led to the ten-fold increase in power density that generated the current enthusiasm for automotive PEMFC's. First, catalyst makers learned to pack ~3x10@super20@ active platinum sites into a cubic cm of porous catalyst layer through the synthesis of ~50% Pt (by weight) catalysts with >25% dispersion on carbon supports with high electronic conductivity. Second, incorporation into the catalyst layer of ionomer similar to that used in the membrane allowed adequate ionic conductivity to be maintained between these active sites and the electrolyte membrane. While the resulting complex nanostructures must maintain some water content to allow ionic conductivity, excessive retention of product water can prevent access of the gaseous reactants to the catalyst particles. The system contains many interfaces: gas/liquid, gas/ionomer, liquid/ionomer, ionomer/metal, metal/carbon, ionomer/carbon (and perhaps gas/metal), all of which must be carefully controlled. Vacuum surface analytical techniques have yielded major clues as to why Pt-alloy catalysts, the enhanced activity of which is necessary if automotive cost targets are to be met, can be stable in the strongly acidic PEMFC environment. Similar analytical successes on water/ionomer/Pt/carbon interfaces are needed to speed progress toward fuel cells that fully meet automotive requirements.

Friday Morning, November 19, 2004

Applied Surface Science
Room 210A - Session AS-FrM

FIB and Novel Ion Analysis Methods
Moderator: F.A. Stevie, North Carolina State University

8:20am **AS-FrM1 Elemental and Surface Analysis Via Focused Ion Beam Induced X-Rays***, **L.A. Giannuzzi**,* FEI Company

Characteristic X-ray emission result from ion/solid interactions, and is the basis for the well known analysis technique referred to as particle induced X-ray emission (PIXE). Characteristic X-rays may be emitted by either bombardment by MeV protons or heavy ions of a few keV. The advantage to heavy ions is that the X-ray yield is confined to a narrow region near the surface. Since the stopping power for < 30 keV Ga+ ions may be orders of magnitude greater than the stopping power for < 30 keV electrons, the acquisition of characteristic X-rays from regions containing both excellent spatial resolution and excellent depth resolution using a focused ion beam (FIB) instrument rather than a scanning electron microscope (SEM) as the primary source are feasible. An additional advantage of heavy ion induced X-ray emission over electron induced X-ray emission is that the Bremsstrahlung is orders of magnitude lower. Thus, ion induced X-ray spectra provides for superior peak to noise ratios, and therefore, offers the possibility for trace element sensitivity compared to electron induced X-ray emission via e.g., X-ray energy dispersive spectrometry (XEDS). In addition, the near surface ion/solid interactions also allow for the possibility of surface analysis via FIB induced X-ray analysis (FIBIX). An added advantage of the FIBIX technique is its sensitivity to soft X-rays, and therefore, light elemental analysis.

8:40am **AS-FrM2 FIB for Materials Characterization, Device Creation and Sample Preparation***, **R.J. Young**,* FEI Company **INVITED**

Focused ion beam (FIB) systems and DualBeam (combined FIB-SEM) systems have become key tools in the high-resolution characterization of materials, most notably in the semiconductor and data-storage industries, but also extending to many other disciplines where localized sample preparation and analysis is required. Site-specific cross-sections and transmission electron microscope (TEM) samples through disparate materials can be prepared using FIB milling. On a DualBeam the SEM can be used to directly monitor the sample preparation, allowing the section to be precisely positioned relative to a sub-surface feature that is exposed during the sample preparation. In addition, high-resolution, high contrast STEM (scanning transmission electron microscopy) imaging is possible with the electron beam, enabling more problems to be solved in the DualBeam without resorting to the TEM. Ion beam and electron beam induced gas chemistry is also possible, enabling the localized deposition of conductors and insulators, and the selective etching of materials. These capabilities are used in characterization applications for surface protection and delineation of cross-section faces, and also allow integrated circuits to be rewired to debug or prototype the device. Similarly, micro- and nano-scale devices can also be created or modified by the FIB/DualBeam, enabling rapid investigations into novel structures that would be impractical to create by other methods.

9:20am **AS-FrM4 High Spatial Resolution XPS Analysis of Focused Ion Beam Irradiated Specimens**, *J.L. Fenton, **K.M. Archuleta**, J.E. Fulghum,* The University of New Mexico*; D.P. Adams, M.J. Vasile,* Sandia National Laboratories

Focused ion beams (FIB) are utilized in applications ranging from the preparation of samples for SEM and TEM analysis to machining of micro-tools. Despite their widespread use, there have been few detailed studies identifying how ion bombardment affects the chemistry of the near-surface region. The goal of this project is to assess the impact of Ga+ resulting from FIB preparation. High energy (30 keV) focused ion beam sputtering was first used to mill >100 µm wide features in Si, C and GaAs substrates. Both quantitative, high spatial resolution imaging and spectra-from-images methods were then used to characterize surface chemical distributions. The Ga distribution on the surface was determined in each case, and the impact of implanted gallium on surface oxidation was evaluated. The change in surface stoichiometry with ion dose (from approximately 10@super 15@ - 10@super 18@ ions/cm2) is also discussed. Atomic force microscopy and TEM have been used to investigate the evolution of morphology with ion dose so to aid the interpretation of XPS data.

10:20am **AS-FrM7 Examining the Impacts of Ion Sputtering on Nanoparticles and Nanoporous Materials***, **A.S. Lea**, M.H. Engelhard, D.J. Gaspar, J.R. Williams, D.R. Baer,* Pacific Northwest National Laboratory

Nanostructured materials of various types and forms are increasingly subject to every type of chemical and physical analysis possible. During the course of studies on several different types of nanostructured materials, we have observed evidence that the extent of damage and material removal rates due to ion sputtering may be significantly different than for continuous films or bulk forms of similar materials. To confirm such effects, we need to know many details about size, size distribution, density, and shape that are not always readily obtained. This presentation will review our efforts to quantify the sputter and damage rates for some nanomaterial systems, including iron oxide nanoparticles and porous silica films. We are working to expand our range of information in more details for these materials and to different types of nano-sized objects. Material removal rates are monitored by XPS and AES and material structure information, including material amounts, is also measured by a variety of methods including TEM, XRD and Nuclear Reaction Analysis.

10:40am **AS-FrM8 Determination of Optimum Depth-Resolution Conditions for Time-Of-Flight Medium Energy Backscattering***, **R.D. Geil**, B.R. Rogers, Z. Song,* Vanderbilt University

Measurements of depth resolution in time-of-flight medium energy backscattering analysis have been made in ErAs and ScAs single crystal films on GaAs (100) as a function of depth, beam energy, and analysis angle using He@super +@ as the analysis ion. Film thicknesses ranged from about 5 Å to 50 Å. Experiments were performed with beam energies ranging from 100 keV to 270 keV with the targets oriented at angles ranging from 5° to 55°. Multiple scattering and straggling effects limited depth resolution at analysis angles near 55° while the resolution of the spectrometer was the limiting factor for angles near normal to the beam. Estimates of depth resolution were made from theoretical calculations and were shown to be in good agreement with experimental values when the analysis angles were small. The departure of theoretical values from experimental measurements can be attributed to multiple scattering events and surface roughness.

11:00am **AS-FrM9 Quantitative Profiling of Thin Films by Means of Elastic Recoil Detection Analysis (ERDA) with High Energetic Heavy Ions***, **W. Bohne**, J. Röhrich, E. Strub,* Hahn Meitner Institut Berlin GmbH, Germany **INVITED**

Heavy-Ion ERDA (Elastic Recoil Detection Analysis) can be used to characterize thin solid layers. The concentrations of chemical elements can be determined as well as the layers' thickness and depth profiles. For the measurement, the sample is irradiated with a heavy ion beam. Atoms of the sample are recoiled and detected with an energy and mass dispersive spectrometer. Since the ERDA principle is based on the classical Rutherford scattering theory, the expected yields for the given conditions can be calculated exactly. Therefore, ERDA is a standard-free method. Absolute concentrations can be determined for all detected chemical elements simultaneously, including hydrogen, with almost the same sensitivity. With the time-of-flight ERDA setup at the Hahn-Meitner-Institut (HMI), there are measured almost 500 samples per year. As a standard projectile beam gold ions with an energy of 350 MeV are used. Typical requests are determination of the stoichiometry, in-depth element distributions, concentration of impurities, and the validation or calibration of data from other analytical methods. Typical artifacts or systematic uncertainties of these methods can be ruled out by comparison with the ERDA data. There will be presented a selection of current ERDA measurements mainly concerning the characterization of materials for thin film photovoltaic devices developed at the HMI. Also a comparison with other analytical methods will be shown. The pros and cons of ERDA measurements will be dicussed.

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