Applied Surface Science

Room 206 - Session AS+BI+NS-MoM

Nanoscale Analysis: Biomaterial and Other Applications

Moderator: A.M. Belu, Medtronic, Inc.

8:20am AS+BI+NS-MoM1 The Development of NSOM for Live Cell Applications, *R.C. Dunn, O. Mooren,* University of Kansas   **INVITED**
Near-field scanning optical microscopy (NSOM) is a scanning probe technique that enables optical measurements to be conducted with nanometric spatial resolution. This technique offers single molecule detection limits, high spatial resolution, and simultaneous force and optical mapping of sample properties. As such, it has found applications in many areas including the study of thin films, polymers, and solid-state materials. Perhaps its greatest potential, however, lies in the biological sciences, where fluorescence techniques are well developed for tagging specific proteins or structures or following dynamic processes such as calcium signaling. To date, NSOM measurements on viable cells remains problematic due to the forces involved in maintaining the tip close to the sample. Our laboratory has been actively developing new methods for conducting NSOM measurements that are amenable with soft and fragile samples such as living cells. We recently reported a new NSOM tip design built around a conventional atomic force microscopy tip that can be used to make high resolution fluorescence measurements on living cells. The development of these techniques and their application to the study of lipid rafts and nuclear pore complexes in the nuclear envelope will be discussed.

9:00am AS+BI+NS-MoM3 Local Mobility in Membranes: Atomic Force Microscopy and Fluorescence Correlation Spectroscopy, *A.R. Burns, D.J. Frankel,* Sandia National Laboratories
The lateral organization and dynamics of lipids and proteins in membranes are critical to cellular signaling processes. Fluorescence imaging and atomic force microscopy (AFM) are both effective ways to map the location and structure of membrane components and domains (e.g., lipid rafts) in supported membranes. Since dynamical processes like translational diffusion of lipids and proteins are dependent on the local membrane structure and molecular interactions, it would be advantageous to correlate dynamics with detailed topography mapped out with AFM. We do this by performing fluorescence correlation spectroscopy (FCS) at specific sites imaged by simultaneous AFM and submicron confocal fluorescence microscopy. We have thus examined the relative partitioning and diffusion coefficients for both tail and head labeled GM1 ganglioside, as well as for head and tail labeled phospholipids, in phase separated domains. Our results indicate significant mobility changes in the micron-scale domains due to differences in lipid packing and ordering. We also observe a large reduction in the mobility of GM1 when bound to cholera toxin B fragments. The effects of membrane proteins will be discussed as well. This research was supported in part by the Division of Materials Science and Engineering, Office of Basic Energy Sciences, U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under Contract DE-AC04-94AL85000.

9:20am AS+BI+NS-MoM4 Molecular Orientation Imaging with sub 10-nm Resolution by Vector Piezoresponse Force Microscopy, *B.J. Rodriguez,* North Carolina State University; *S. Jesse, A.P. Baddorf,* Oak Ridge National Laboratory; *A. Gruverman,* North Carolina State University; *S.V. Kalinin,* Oak Ridge National Laboratory
Functional properties of calcified and connective tissues are determined by the relative ordering and orientation of a relatively small number of biopolymers, such as collagen. Here we present a new approach for local molecular orientation imaging in biological systems by Vector Piezoresponse Force Microscopy (Vector PFM). Vector PFM is capable of determining the local electromechanical activity and orientation in piezoelectric materials with a spatial resolution below 10 nm. The applicability of Vector PFM to biological systems is demonstrated for objects from butterfly wings to bones. Electromechanical characterization of enamel and dentin layers in human tooth is demonstrated. The vector electromechanical response of a bundle of collagen molecules in human tooth dentin has been visualized with 5 nanometer resolution. A method for imaging the local orientation of biomolecules from Vector PFM data has been illustrated using collagen molecules embedded in a hydroxyapatite matrix. As another example, 2D piezoelectric properties and local elasticity of a butterfly wing are measured with nanoscale resolution and interpreted in terms of the relative orientation of chitin molecules in the wing scales. The ubiquitous presence of electro-activity in biopolymers, such as chitin,

keratin, collagen, and cellulose, suggests that Vector PFM has exceptional potential for orientation imaging of biological materials on the sub-10 nanometer length scale. Research was sponsored by the U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC and by the National Science Foundation grant DMR-0072998 (AG). Research partially performed as a Eugene P. Wigner Fellow (SVK).

9:40am AS+BI+NS-MoM5 Nanoscale Raman and Fluorescence Microscopy of Carbon Nanotubes, *A. Hartschuh, H. Qian, A.J. Meixner,* University of Tuebingen, Germany; *N. Anderson, L. Novotny,* University of Rochester   **INVITED**
Spectroscopic methods with high spatial resolution are essential for understanding the physical and chemical properties of nanoscale materials including biological proteins, quantum structures and nanocomposite materials. Optical techniques are of special interest because the energy of light quanta is in the range of electronic and vibrational transitions. Advances in near-field optics open up new means to overcome the diffraction limit and extend the range of optical measurements to the length scales of most nanosystems. Recently, a near-field optical technique based on local field enhancement has been demonstrated which allows to perform spectroscopic measurements with 20 nm spatial resolution.@footnote 1,2@ The method makes use of the strongly enhanced electric field close to a sharp metal tip under laser illumination. In this approach the metal tip is held a few nanometers above the sample surface so that a highly localized interaction between the enhanced field and the sample is achieved. Raster scanning the sample then allows for simultaneous optical and topographic imaging. Single-walled carbon nanotubes (SWCNTs) have been the focus of intense interest due to a large variety of potential nanotechnological applications. We demonstrate near-field Raman and fluorescence imaging of the same individual single-walled carbon nanotube and show that a spatial resolution of less than 20 nm can be achieved. The high-resolution capability and chemical specificity of the presented method is used to study local variations in the optical spectra of SWCNTs which would be hidden in farfield measurements. The technique has great potential for becoming a routine tool for the chemical analysis of surfaces at high spatial resolution. @FootnoteText@ @footnote 1@ E. J. Sanchez et. al, Phys. Rev. Lett. 82, 4014 (1999).@footnote 2@ A. Hartschuh et. al, Phys. Rev. Lett. 90, 095503 (2003).

10:20am AS+BI+NS-MoM7 Scanning Atom Probe Study of Fragmentation of Organic Molecules, *O. Nishikawa, M. Taniguchi,* Kanazawa Institute of Technology, Japan
Fragmentation of two organic molecules, crystal violet [(C@sub25@N@sub3@H@sub30@)@super+@Cl@super-@: 408 amu] and tetra-n-butyl-ammonium hydroxide [N(C@sub4@H@sub9@)@sub4@@super+@OH@super-@: 259 amu], was studied at atomic level by mass analyzing the dissociated fragments with the scanning atom probe (SAP). In the SAP analysis the molecules and their fragments are field evaporated as positive ions and detected one by one. Since the field evaporation is a static process, it does not disorder surface structure breaking atomic bonds by external energy. Accordingly, evaporated positive ions reflect the binding state in the molecules. For example, the radical of polythiophene, SC@sub4@H@sub2@, is field evaporated as doubly charged ions indicating that the atoms forming the radical are strongly bound. A thin layer of crystal violet was deposited on a tungsten substrate. Since the crystal violet is non conductive, the molecules are field evaporated applying a DC high voltage to the tungsten substrate and irradiating the specimen with a pulsed laser beam, 2nd harmonic of YAG laser, 532 nm. Although non-dissociated molecule ions are detected, most molecules are dissociated showing the ions such as C@sub13@H@sub2@, C@sub13@NH@sub4@ and C@sub8@NH@subn@. The detected fragments suggest that no double bonds are broken. When the molecule layer was deposited on a titanium oxide layer, all molecules were dissociated possibly due to the photo-catalytic function of titanium oxide. The most abundant fragment is C@sub4@NH@subn@. The ratio of the number of carbon atoms to that of nitrogen atom was found to be nearly 8:1 as expected. Although the dissociation of tetra-n-butyl-ammonium hydroxide molecules at the boundary with the tungsten substrate is noticeable, the dissociation is insignificant at non-boundary areas. It was also found that hydroxide of the molecules is dissociated and oxygen atoms are bound with tungsten. This may suggest that tungsten also have catalytic function.

10:40am AS+BI+NS-MoM8 Surface Potential Mapping of DNA-protein Complex at Molecular Level, *E. Mikamo, F. Yamada, T. Matsumoto, T. Kawai,* Osaka University, Japan

Atomic force microscopy (AFM) is a valuable method for the study of biomolecules such as DNA, RNA and proteins at real-space. The biomolecules have generally been adsorbed on the insulating substrate as mica to observe by AFM. However, it is very hard to measure the local electric properties of the insulating substrate and the conductive substrate has been commonly used. Recently our group demonstrated the measurement of electric properties of DNA and Au nanoparticles on mica and sapphire substrate. This result encouraged us to measure the complex of biomolecules on the insulating substrate at molecular level. We report here surface potential and capacitance measurement of DNA, protein and DNA-protein complex on the insulating substrate. The experiments are based on frequency mode non-contact AFM (FM-ncAFM). The FM-ncAFM is able to detect the high-sensitive local electrostatic forces and prevent the charge injection caused by tip-sample contact. We observed the surface potential mapping and topographic image simultaneously. The topographic images clearly showed DNA and protein as line and dot structure. The surface potential of corresponded structures is observed as bright contrast. Our results indicate that surface potential of DNA, protein and DNA-protein complex is higher than insulating substrate surface. The potential images resolve the double strand DNA, thin structure less than 2 nm, and protein at single molecular revel. To estimate the capacitance of individual molecules, we measured d(@DELTA@F) per dV images. The measurement of surface potential and capacitance indicate that this technique is able to discriminate the individual molecules on an insulating substrate. This work was supported by grants from the New Energy and Industrial Technology Development Organization (NEDO).

11:00am AS+BI+NS-MoM9 The Importance of Aberration Corrected SEM and TEM to the Semiconductor Industry, *A.C. Diebold,* SEMATECH & AMRC, US; *B. Foran,* ATDF & AMRC; *M.J. Yacaman, B.A. Korgel,* University of Texas & AMRC **INVITED**

Microscopy continues to be a critical need for the semiconductor industry. Feature sizes continue to shrink with logic having a two-year cycle for introduction of each new technology generation. Over the next fifteen years, the gate length of transistors will rapidly shrink to less than 10 nm. The interconnect technology connecting the transistors will keep pace with this size reduction. Research and development needs occur well ahead of manufacturing needs. Thus, there already is a need for microscopy capable of imaging and characterizing the interfaces, film layers and structures for future devices. Recent advances in electron optics technology have corrected for chromatic and spherical aberrations that have long limited resolution in scanning electron microscopy (SEM) and tranmission electron microscopy (TEM). Commercially available advances include monochromators to reduce the energy spread of the electron source and lens correctors to reduce spherical aberration. Resolution of state of the art scanning TEM and High resolution TEM has been proven below 0.1 nm. Aberration correction technology is also now commercially available for SEM and allowing resolution to 0.6 nm. In this paper we discuss the advances in imaging that aberration corrected lenses have enabled along with semiconductor industry applications. We will discuss near-term applications such as the characterization of interfaces in the transistor gate stack and measurement of strain in the transistor channel, and then also discuss long-term research applications such as nanowires and nanodots. Abberation correction will not solve all microscopy problems, and we will discuss specific cases such as sample or analytical limitations that can obviate any benefit of aberration correction technology.

11:40am AS+BI+NS-MoM11 Scanning Tunneling Microscope Assisted with Inner-Shell Excitation by Hard X-ray Micro-Beam, *A. Saito,* Riken Harima Inst., Japan; *J. Maruyama, K. Manabe,* Osaka Univ., Japan; *K. Kitamoto,* Riken Harima Inst., Japan; *K. Takahashi,* Osaka Univ., Japan; *Y. Tanaka,* Riken Harima Inst., Japan; *M. Yabashi, M. Ishii,* Japan Synchrotron Radiation Res. Inst.; *M. Akai-Kasaya,* Osaka Univ., Japan; *S. Shin, T. Ishikawa,* Riken Harima Inst., Japan; *Y. Kuwahara, M. Aono,* Osaka Univ., Japan

A scanning tunneling microscope (STM) system was developed for in-situ experiments under the irradiation of highly brilliant hard x-rays of synchrotron radiation (SR). It appears attractive to excite the core electrons of specific level under the STM observation, because it may enable to analyze the elements or control the local reaction with the spatial resolution of STM. To surmount a small probability of the core-excitation by hard X-rays, SR of the highest brilliance at the SPring-8 was used. To prevail the difficulties produced by the highly brilliant SR (damage around the STM scanner, thermal and electrical noise, and instability of the system such as thermal drift), the beam size was limited to @phi@10 μm. The small beam size serves also to obtain a high signal to noise ratio and high spatial resolution by restraining the electrons emitted from a wide area. The in-situ STM observation was enabled by developing an accurate "three-body (invisible micro-beam, tip-end, and sample surface)" alignment system in ultrahigh vacuum. Despite a noisy condition of SR facility and radiation load around the probe tip, STM images were successfully obtained with atomic resolution. The analysis of the clean Si(111) surface revealed that the thermal expansion affects to the behavior of the tip much strongly than reported in the past reports. Next, the tip-current spectra were obtained on Ge nano-islands on the clean Si(111) surface, by changing the incident photon energy across the Ge absorption edge. A current modification was detected at the absorption edge, with a spatial resolution of the order of 10 nm. This system will serve to observation or manipulation with atomic resolution, which is based on the interaction between the surface atoms and the hard X-ray photons.

Monday Afternoon, October 31, 2005

Applied Surface Science
Room 206 - Session AS-MoA

Electron Spectroscopies
Moderator: R.L. Opila, University of Delaware

2:00pm AS-MoA1 High Resolution XPS and EELS of Assembled Organic Monolayers, *J.-J. Pireaux*, University of Namur, Belgium **INVITED**
Everyday application of XPS allows to unravel with quite simple procedures the elemental and chemical composition of materials surface in a quantitative way. Core and valence band spectra analyses do contain structural information as well : to gather it, high resolution analysis and sometimes study of reference materials are necessary. This will be demonstrated with the determination of the good-or-bad assembling property of some silane molecules with different hydrocarbon chain length deposited from a solution onto TiO@sub 2@ single crystals ; a model of the -Si-O-Ti-O- interfacial layer will be presented. While XPS and UPS synchrotron photoemission valence band analysis remain still qualitative for the determination of structural order, we will show that high resolution electron energy loss spectroscopy[(HR)EELS] can been successufully used to evaluate the crystalline domain size of alkane thiols layers assembled on gold surfaces ; indeed, the measure of the angular distribution of the scattered electrons corresponds to a diffraction experiment. With contributions of R. Magnée, Ch. Grégoire and A.-S. Duwez

2:40pm AS-MoA3 Evaluation of Electron Back-scattering in Auger Analysis using a Cross-sectioned GaAs/AlAs Superlattice, *M. Suzuki*, N. Urushihara, S. Iida, N. Sanada, ULVAC-PHI, Inc., Japan; *D.F. Paul, J.S. Hammond,* Physical Electronics; *A. Yamamoto,* ULVAC-PHI, Inc., Japan
It is generally well known that when using electron excitation analysis techniques such as Auger electron spectroscopy, the analyzed volume is expanded due to the scattering effects in a solid surface region. We will present experimental results to evaluate generation of Auger electrons by inelastic scattered electrons. A cleaved cross-section of a GaAs/AlAs superlattice, consisting of three different thicknesses of repeating layers of GaAs/AlAs (50 nm/50 nm, 20 nm/20 nm, and 10 nm/10 nm) was analyzed with a scanning Auger Nanoprobe. Along the analyzed line perpendicular to the 50 nm thick-layers, the kinetic energy of the Al KLL Auger electrons varied by 5 eV to 6 eV, with a spatial distribution corresponding with the GaAs/AlAs superlattice structure. The amplitude of the Auger peak energy shift with beam position was smaller for the 20 nm-thick layers and almost negligible for the 10 nm-thick layers. The highest and lowest Auger energy positions correspond to the AlAs and GaAs layers, respectively. The analyzed surface was covered with a naturally oxidized layer, as the cleavage was carried out in air. The lower Al kinetic energy signal was detected when the electron beam hit the AlAs region, due to the reduction of aluminum oxide caused by electron beam.@footnote1@ The higher Al kinetic energy signal associated with aluminum oxide was generated by inelastically scattered electrons when the beam was at the GaAs region. These results will be discussed based on a model of electron scattering. @FootnoteText@ @footnote1@ M. Arai et al., O-32, The third international symposium on practical surface analysis (PSA-03), Korea, October 2003.

3:00pm AS-MoA4 Angle Resolved XPS for Characterization and Metrology of Ultra-Thin Silicon Oxynitride Films, *C.R. Brundle,* C. R. Brundle & Associates; *G. Conti, Y. Uritsky,* Applied Materials, Inc.; *P. Mack,* Thermo Electron Inc., UK
The analytical tool set used in the wafer processing industry for metrology of thin films is changing because the films are becoming so thin and more complex. One of the new contenders for both characterization (the kind of detailed information needed in development, trouble shooting, and failure analysis) and metrology (rapid measurements of specific parameters on large numbers of samples) is XPS. Whereas many of the techniques used in the past become less effective as films become ultra-thin (0 to 50A range), XPS becomes most effective in this range. For the high k dielectric material, SiON, as used in the current generation of gate oxide production (10 to 30A), Angle Resolved XPS can provide very precise film thickness and at the same time, in principle, provide a depth distribution of the nitrogen dose using a constrained model to fit the data. Since the model fit to the data can never be unique the approach works best for two extremes: 1) when there are really gross differences in distributions between films and it is this qualitative difference one is looking for and 2) when there are multiple measurements available for films made under a given processing condition that give the same profile fit, and then multiple measurements under a different processing condition which give a consistently different fit (even if

small), signifying that a change in profile has occurred. We present examples of both situations from current industry samples. The former is more of a film/process development issue and the latter is more of a metrology issue. It does seem possible to tell that small changes in distribution have occurred, even if one cannot fully quantify those changes. An interesting point is that in none of the many (hundreds)of samples studied, is a spike in the N concentration observed at the surface (first 2A) by ARXPS, unlike in some reports using TOFSIMS on similar samples.

3:20pm AS-MoA5 Multi-Technique Characterization of Iron Nanoparticles, *D.R. Baer*, M.H. Engelhard, C.M. Wang, K.H. Pecher, Pacific Northwest National Laboratory; *R.L. Penn,* University of Minnesota; *P.G. Tratnyek,* Oregon Health and Sciences University; *Y. Qiang,* University of Idaho; *D.E. McCready, J.C. Linehan, J.E. Amonette,* Pacific Northwest National Laboratory; *J. Antony,* University of Idaho
Understanding the chemical properties of iron nanoparticles requires detailed information about the size, physical and chemical structure and the presence of surface coatings. Because of the reactive nature of iron, these particles are usually covered by some type of incidental or deliberately added protective layer. In spite of any protection, the properties of the particles change with time and are altered by the environments they have been exposed to and in some cases by the manner the samples have been handled prior to analysis. For some of our reaction studies, we expect the particles to react and change with time and it is important to understand this particle evolution. This presentation will describe aspects of nanoparticle synthesis and processing, the methods we are using to handle the samples, the priority and order of the analysis, and the information we expect from each method. Methods routinely used include: x-ray photoelectron spectroscopy; transmission electron spectroscopy; x-ray diffraction; surface area analysis; x-ray adsorption spectroscopy. These are correlated with measurements of electrochemical properties and chemical properties. The issues and challenges of forming a consistent picture of the particles as a function of time will be discussed.

3:40pm AS-MoA6 Workfunction Differences between Cu Grains: Laterally Resolved UPS with the NanoESCA, *J. Westermann*, D. Funnemann, B. Kroemker, Omicron NanoTechnology GmbH, Germany
Recently, we have developed an Imaging XPS spectrometer with lateral resolution in the range of 200nm and below.@footnote 1,2@ This instrument has recently been used for the study of work function differences on a variety of samples. Main focus of this application was the work function variation between different copper grains. As copper is currently of great interest as a material for interconnects in semiconductor devices, the understanding of grain properties is a key for the improvement of the interconnect properties. Samples were provided by the Laboratoire d'Electronique de Technologie de l'Information (LETI, Grenoble). Using the NanoESCA, we can show for the first time the relation between secondary electron intensity and work function with a high spatial resolution. Surprisingly, this does not follow the Fowler plot as was expected previously.@footnote 3@ In addition, we show measurements on a heterogenous material combination with microstructured Gold patterns on a Silicon Oxide sample. These data demonstrate the powerful combination of imaging with spectroscopy: We identify regions of band-bending, charging and different work-functions. @FootnoteText@ @footnote 1@ Escher et al., J.Phys.:Condens. Matt 17 (2005) 1329-1338@footnote 2@ Escher et al., J. Electron Spectrosc. Relat. Phenom., 144-147 (2005) 1179-1182@footnote3@ Przychowski et al., Surf. Sci. 549 (2004) 37-51.

4:00pm AS-MoA7 In-Situ and Ex-Situ Characterization of the Electrochemically-Accelerated Corrosion of Ni-Cr-Mo-Gd Alloy Surfaces in Aqueous Media, P.J. Pinhero, T.E. Lister, R.E. Mizia, *T.L. Trowbridge,* Idaho National Laboratory; *A.W. Glenn,* Idaho Completion Project
A new thermal-neutron-absorbing structural Ni-Cr-Mo-Gd alloy was developed at the Idaho National Laboratory (INL). The purpose of this alloy is to potentially absorb neutrons liberated from spent nuclear fuel (SNF) and mitigate any issues related to nuclear criticality. The microstructure of this alloy indicates a two-phase structure consisting of the primary Ni-Cr-Mo austenite matrix phase and secondary Ni@sub 5@Gd phase inclusions arising from the precipitation of the austenite-insoluble Gd. Presently, this alloy is under consideration for use within the U.S. Department of Energy (DOE) standardized SNF waste packages. To support the case for this alloy's acceptance and understand its more fundamental surface character, studies were undertaken to examine its structure and composition with respect to its bulk properties, the role of oxidation and resulting passivation on its susceptibility to corrode, and finally how these properties are influenced through boron-doping. This paper focuses on the

susceptibility of the Ni-Cr-Mo-Gd surface to corrode. Scanning electrochemical microscopy (SECM) was used to examine localized corrosion of the surface in situ. It was observed that the corrosion initiates at the interfaces between the Ni@sub 5@Gd particles and the surrounding austenite matrix. Corrosion then propagates such that these particles completely dissolve, leaving an intact "passive" Ni-Cr-Mo surface. Current-sensing atomic force microscopy (CS-AFM) images help support the argument of electron transfer initiating at the interface formed between the included particles and the austenite matrix. Ex situ analysis using focused ion beam / scanning electron microscopy (FIB/SEM), scanning Auger microscopy (SAM), and x-ray photoelectron microscopy show how the structure and surface composition change as a function of the electrochemically driven corrosion process.

4:20pm **AS-MoA8 Throughput Advantages of PRBS Modulation in TOF Electron Spectroscopy and Mass Spectrometry**, *R.H. Jackson,* Stillwater Scientific Instruments*; Z. Yang,* Univ. of Maine*; L.J. LeGore, B.G. Frederick, P.H. Kleban, C.B.H. Crothers, D.P. Martin,* Stillwater Scientific Instruments
Pseudo-random binary sequence (PRBS) modulation is a method of multiplexing in the time domain to increase the time domain efficiency of an analyzer. We have combined PRBS modulation in a time-of-flight velocity analyzer with maximum likelihood signal recovery methods in both high resolution electron energy loss spectroscopy (HREELS) and mass spectrometry (MS). In previous TOF-HREELS measurements, we have decreased data acquisition times from hours per spectrum to a few minutes, while maintaining resolution in the 2-4 meV range. Although time-of-flight instruments typically trade improvements in time domain throughput for decreases in the etendue, the use of a Bradbury-Nielsen gate chopper allows our optical design to maintain large acceptance angles from the source while achieving high throughput and resolution. We characterize the throughput advantages of a broadband input lens for use in the TOF-HREELS analyzer. Similar advantages are achieved in our GC/MS implementation of a TOF mass spectrometer, compared to the state-of-the-art orthogonal acceleration TOF-MS configuration. We also report order of magnitude improvements in the time resolution and throughput of the timing and control electronics and computational capabilities for implementation of the data recovery algorithms.

4:40pm **AS-MoA9 Novel Field Emission Source for Electron Microscopy**, *J.W. Lewellen, **J.R. Noonan**,* Argonne National Laboratory
A novel field emission electron source that combines desirable features of thermionic cathode and photocathode has been designed. Simulations indicate that the electron beam has very small emittance, ~ 2 nm-radian, and high average current. The emittance can be reduced to less than 0.01 nm-radian by taking beam slices, which also reduces the beam current. The source uses high gradient radio frequency (RF) fields to extract electrons off of a field emitter tip and accelerate these electrons to ~1.5 MeV energy. The resulting gun design show promise in a number accelerator and non-accelerator applications, such as energy recovery LINACS, TeraHertz radiation sources, high voltage electron microscopy, electron beam welding, and thin film deposition. This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract No. W-31-109-ENG-38.

5:00pm **AS-MoA10 Differential Charging of Nanoparticles on Oxide Surfaces as Determined by XPS with External Stimuli**, *U.K. Demirok, I. Tunc, **S. Suzer**,* Bilkent University, Turkey
By recording the XPS spectra while applying external d.c. and/or pulsed voltage stimuli, it is possible to control the differential charging, and extract information related with dielectric properties of various surface structures. We have carried out a number of experiments to determine the charging/discharging behavior of various surface structures consisting of Au, Ag, and Pt (metallic), Titania (semiconductor), and Silica (dielectric) both as they are and also as Core-Shell type Nanoparticles using XPS with external voltage stimuli. Differences and similarities of these structures with respect to their chemical compositions, and also with respect to the form (d.c., pulsed, etc.) of the voltage stimuli applied, will be presented and discussed in detail.

Applied Surface Science
Room Exhibit Hall C&D - Session AS-MoP

Aspects of Applied Surface Science Poster Session

AS-MoP2 Unusual Interdiffusion Reactions in Multilayer ZrO@sub 2@CaO/Fe/Si Thin Films, *H. Piao, L. Le Tarte, L. Denault, J.R. Cournoyer, K. Dovidenko, M. Larsen, J. Osaheni,* General Electric Co., Global Research Center

Interdiffusion reactions in multilayer ZrO@sub 2@CaO/Fe/Si thin film (2mm diameter dot) have been studied using X-ray Photoelectron Spectroscopy (XPS) in combination with Scanning Auger Microscopy (SAM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). The 2mm diameter thin film dots were prepared through a shadow mask by depositing Fe and ZrO@sub 2@CaO sequentially on silicon substrates, followed by thermal treatments. It was found that heating at elevated temperatures resulted in the segregation of the islands on the substrate with the accompanying formation of irregular shaped pits in the film. The diameters of the islands are typically in the range from 100 to 250nm. XPS and SAM results on these islands indicated that the islands are mainly iron silicide coated with Fe, Zr-Ca and Si oxide towards to the surface. The formation of the interfacial iron silicide (FeSi@sub 2@) arising from the bulk interdiffusion of Fe and Si were confirmed by XPS, TEM, and SAD (selected area diffraction) studies. Much more surprising is the surface enrichment of silicon oxide on the whole dot surface. The fast segregation of silicon from the substrate to the surface does not appear to be via bulk interdiffusion. The implications of these findings to the diffusion properties of the thin film will be discussed.

AS-MoP3 Synthesis and Characterization of Spectroscopic Tags Based Surface-Enhanced Raman Spectroscopy (SERS) of BPE Adsorbed on Gold Nanoparticles, *M.C. Burrell,* GE Global Research Center

Nanoparticle tags detectable by Raman spectroscopy, due to the surface-enhanced Raman effect (SERS) of adsorbed reporter molecules, have potential applications ranging from biological assays to cellular imaging. This paper describes the surface chemistry considerations, and characterization methods employed, in producing gold nanoparticles with an adsorbed bis(4-pyridyl) ethylene [BPE] reporter molecule. The SERS response of the tags is affected by the size of the gold nanoparticles, the adsorption conditions of the BPE, and co-adsorption of precursors for growth of protective shells. A primary consideration in producing tags is preventing aggregation of the particles, even though the SERS enhancement of individual particles is lower than aggregates. We will present data from Raman spectroscopy, UV-visible absorbance, light scattering, and TEM to used to characterize the tags during the synthesis process.

AS-MoP4 Dimensional Effects of Metal Nanoparticles on Their Characterization by X-ray Photoelectron Spectroscopy, *D.-Q. Yang, E. Sacher,* Ecole Polytechnique of Montreal, Canada

X-ray photoelectron spectroscopy (XPS) has been found very useful in the understanding of the electronic states of supported metal catalyst nanoparticles. We give a short review on the photoelectron emission behaviour of nanoparticles deposited on several relatively unreactive substrate surfaces, including highly oriented pyrolytic graphite (HOPG) with varying surface defects densities, and low permittivity polymers. We fix our attention on the (1) photoelectron emission yield enhancement induced by the nanoparticles, (2) photoelectron emission from the shell and the core of the nanoparticles, (3) size-dependent binding energy shifts, (3) Auger parameters, (4) Wagner plots and (5) initial-state and final-state effects on the nanoparticle dimensions and their substrate surface interactions. Intensity ratios, from a given nanoparticle at two different kinetic energies, as well as from nanoparticle and substrate, and their dependences on nanoparticle dimensions, are also explored.

AS-MoP5 Thickness Measurement Of Diamond-Like Carbon (DLC) By Auger Electron Spectroscopy (AES), *Y. Zheng, B. Lu,* Seagate Technology (RMO) Ltd*; G. Selvaduray,* San Jose State University

Abstract-To increase the density of magnetic recoding disks and to protect the magnetic layers from sliding contact and corrosion, it is important to be able to accurately measure the thickness of DLC films. The ability to use AES to measure the DLC thickness on magnetic recording disks was studied. The principle of DLC thickness measurement was based on Beer-Lambert's law. The approach was to construct a working curve by using the thickness of DLC measured by ESCA and the intensities of the carbon and cobalt signals detected by AES to generate the calibration parameter " ". This study demonstrated that the DLC thickness could be measured by AES, employing the intensities of the cobalt signal present in the magnetic layer. Statistical analyses verified that there were no significant differences between the DLC thickness measured by ESCA and those measured by AES.

AS-MoP6 Structural Analysis of a DTHXBQ/Pt(dmg)@sub 2@ on KBr Plate used by TRXPS, *T. Tazawa, Y. Iijima,* JEOL Ltd., Japan*; S. Isoda,* Kyoto University, Japan

Recently, with development of thin film technique, analysis of the molecular film which did lamination in a structural analysis of monomolecular film and thickness of several nm has been demanded from X-ray photoelectron spectrometer (XPS). Because this material is formed on flat plate, such as silicon wafer, it is possible to measure with total reflection x-ray photoelectron spectrometer (TRXPS). A location of standing wave changes when it changes in X-ray incidence angle in TRXPS. This change does intensity change of photoelectron intensity, and it is observed. Variation that is to say occurs in photoelectron intensity by an entity location, a difference of angle in the same functional group. Firstly film formation did Pt(dmg)@sub 2@ in thickness of 15nm on KBr plate by this study, and DTHXBQ film (organic compound) formed on that film, after that we measured this organic compound film used by TRXPS. Measurement changed incidence X-rays from 10° to 0°, and we measured photoelectron intensity-dependence of Pt4f, O1s, C1s and N1s for incidence angle of x-ray. The insturment which we used for measurement is JPS-9200 (JEOL Ltd.). Measurement condition is as follows. Excitation x-ray is AlK@alpha@ monochromatic X-ray, x-ray power in measurement is 300W, and energy resolution is 0.8eV. As a result, we were able to decided a location of Pt in Pt(dmg)2,and a structure of Pt(dmg)@sub 2@ and DTHXBQ films on KBr plate.

AS-MoP7 Investigation of Pharmaceutical Packaging Materials using XPS and TOF-SIMS, *X. Dong, R.G. Iacocca, J. Janimak, M.C. Allgeier,* Eli Lilly

The surface composition of packaging materials is of great interest to the pharmaceutical community because of potential interactions between the packaging surface and the drug product. The surface sensitivity of XPS and TOF-SIMS makes these techniques ideally suited to the surface characterization of packaging materials. In this work, XPS was utilized to evaluate surface compositions of three Type I glass vials from different sources. The bulk compositions of three glass vials are similar to each other, and the surface of one glass vial is ammonium sulfate treated. To thoroughly understand the surface composition, survey and high resolution spectra, as well as small spot images, were collected from all three samples. The XPS results revealed marked difference in surface compositions of the three vials. Significantly higher amounts of B and Na were detected on one vial than on the other two, suggesting that this glass had been exposed to excessive heat. Sodium sulfate residues were present on the ammonium sulfate treated vial, suggesting the rinsing process performed by the manufacturer is not thorough enough. In addition to glass vials, plastic liners, another commonly used packaging material for Active Pharmaceutical Ingredient (API) powders, were also examined. API stored in plastic liners under different conditions were investigated, and compared to that stored in glass vials using TOF-SIMS. It is obvious that the additives present on the surface of the plastic liner were transferred to the API during storage. The preliminary results also suggest that the increase of additives on the API is consistent with the decrease in surface area. This work clearly demonstrates that XPS and TOF-SIMS are highly valuable techniques in evaluation of pharmaceutical packaging materials, as well as in the investigation of the interactions between drug products and the packaging.

AS-MoP8 Determination of Equivalent Circuits of Surface Structures for XPS Analysis, *O. Tasci, U.K. Demirok, E. Atalar, S. Suzer,* Bilkent University, Turkey

XPS analysis of non-conducting samples is usually hampered due to charging, and a great deal of effort has been devoted to minimize it. However, it is also possible to utilize this charging to extract information related with dielectric properties of various surface structures. Determination of equivalent circuit(s) and testing on real samples emerge as essential parts of this analysis. To this end, we have carried out a number of experiments to determine the charging/discharging behavior of various surface structures consisting of Au, Ag, and Pt (metallic), Titania (semiconductor), and Silica (dielectric) Nanoparticles deposited on SiO@sub 2@/Si substrates by XPS. We have also constructed the corresponding equivalent circuits by using the PSPICE program and correlated the output with the experimental data. Our experimental results and their correlation with the model(s) will be discussed in detail.

AS-MoP9 Scanning Probe Microscopy and X-ray Photoelectron Spectroscopy Investigations of Focused Ion Beam-Irradiated Targets, *K. Archuleta,* Sandia National Laboratories*; J.L. Fenton,* University of New Mexico*; M.J. Vasile, S. Campin, D.P. Adams,* Sandia National Laboratories*; J.E. Fulghum,* University of New Mexico

Focused ion beam (FIB) techniques have a wide range of applications, from lithographic mask repair and semiconductor analysis to machining of microtools. As FIB prototyping methods are extended to the nanometer scale, the effects of distributed charge resulting from ion implantation/sputtering, modifications in near-surface chemistry, and evolved surface morphology become more relevant to device fabrication and operation. Toward this end, we investigate the residual electronic and chemical properties of ion-exposed areas. High energy (30 keV) focused ion beams are used to expose 100 Âµm wide features in Si, SiO2 and C substrates. Samples are then removed from the FIB system, and the residual surface potential and spatial distributions of charge are analyzed using ex-situ scanning surface potential microscopy and scanning capacitance microscopy. Changes in residual surface potential are evaluated over a large range of ion dose (~1016 -1018 ions/cm2); this includes conditions that lead to target swelling (low fluence) followed by constant-rate sputter erosion (high dose). The evolving chemistry of the near-surface region is also investigated as a function of ion dose. High spatial resolution, x-ray photoelectron spectroscopy provides insight into the changes of near-surface composition that occur during increased gallium ion exposure.

AS-MoP10 The Efficacy of Organosilane Surface Modifications on Distribution of Polar Inorganic Particles within a Nonpolar Polymer Matrix, *A.K. Wertsching, T.L. Trowbridge, P.J. Pinhero,* Idaho National Laboratory

Improving the surface interface of nonpolar and polar materials is critical to creating the desired physical properties of hybrid composites. Modification of inorganic particles with various organosilanes has the effect of creating a nonpolar surface on a polar material, which then can be dispersed into nonpolar media. However, choice of organosilane can have radically different results on the composite. The impact of the organosilane upon these composites are examined using scanning electron microscopy (SEM), atomic force microscopy (AFM), scanning Auger microscopy (SAM), and x-ray photoelectron spectroscopy (XPS).

AS-MoP11 Accurate Force Measurements in the AFM: Improvements in the MEMS Electrical Nanobalance Calibration Device, *J. Portoles,* National Physical Laboratory and University of Nottingham, UK*; P.J. Cumpson,* National Physical Laboratory, UK*; S. Allen, S. Tendler, P. Williams,* University of Nottingham, UK

Since its invention in 1986 the AFM technique has been a powerful imaging tool, and increasingly an instrument to measure forces of the order of pN to nN. These measurements are important in biological research in the context of the study of specific interactions that affect stability and biological function of macromolecules. The accuracy of those measurements relies largely on the determination of the AFM-cantilever spring constant. Several calibration methods have been developed based on different approaches ranging from dimensional measurements of cantilevers, or static loading to dynamic measurements and Finite Elements simulations. All these methods suffer from poor precision arising from different sources (limited manufacturing control in thickness and elastic properties, difficulties in dynamic modelling, etc) Here a different approach is tested, which doesn't rely on the study of the cantilever systems. All the difficulties concerning elastic constant calibration are "transferred" to a reference system, the Electrical Nanobalance device.@footnote 1@ This is designed as a MEMS device in order to provide accurate calibration of its spring constant by a combination of interferometrical measurements and electrical excitation in vacuum. Once calibrated the spring constant of cantilevers of different materials and geometries can be determined by comparison with the nanobalance device through a simple force-distance measurement performed in air. In this poster we present tests of Electrical Nanobalance MEMS devices, in particular examining the so-called corner-loading problem. @FootnoteText@ @footnote 1@ P J Cumpson and J Hedley, Nanotechnology 14 (2003) 1279-1288.

AS-MoP12 An Investigation of Photoperturbation Effects on Conductive Atomic Force Microscopy, *M.-N. Chang, C.-Y. Chen,* National Nano Device Laboratories, Taiwan

Conductive atomic force microscopy (C-AFM) with a high current sensitivity and a high spatial resolution has attracted much interest in mapping two-dimensional current distribution, investigating the local current-voltage characteristics and examining the breakdown properties of the dielectric layer in electronic devices. With atomic force microscopic setup, C-AFM can synchronously provide the current images and the corresponding topographic images. However, it has been revealed that the stray light of AFM laser beam can induce photoperturbations and hence lead to many difficulties in employing scanning capacitance microscopy to investigate carrier distribution and electrical junctions. In this work, we have qualitatively revealed that the AFM laser beam can significantly perturb the local current-voltage spectra and current distribution profiles taken by C-AFM. Studied samples were n- and p-type silicon covered with a thermally grown ultrathin SiO@sub 2@ film. The wavelength of the AFM laser ranges from 620 nm to 690 nm and the output power is 1.0 mW. The C-AFM measurement was performed in an environment with well-controlled temperature and humidity. For p-type sample, it is clearly observed that the onset voltage decreases with the photoperturbation level. The photovoltaic effect and the additional minority carrier density at the edge of the space-charge region can enhance the electric field across the SiO@sub 2@ film. For n-type sample, photoperturbations can lead to a higher injection barrier height for electrons. Experimental results indicate that the photoperturbations induced by the AFM laser beam not only significantly affects the current image of C-AFM, but also reduces the accuracy of the examination of the current-voltage characteristics, in particular for the ultrathin dielectric film on lower band-gap semiconductors, e.g., Si and Si@sub x@Ge@sub 1-x@.

AS-MoP13 Random Fractal Behavior of InGaAs Quantum Dots Using AFM, *X. Qian, S.R. Vangala, C. Santeufemio, W.D. Goodhue,* University of Massachusetts*; Y. Park,* Inje University, South Korea

Autocorrelation, height-height difference correlation, and power spectral density (PSD) analysis techniques have been applied to AFM scans of semiconductor materials for years. Recently Fenner et al@footnote 1@ and Krishnaswami et al@footnote 2@ have developed and applied random fractal analysis techniques to AFM image statistics in order to determine the fractal nature of semiconductor surfaces. Here random fractals are used to investigate InGaAs quantum dots. An uncapped single layer InGaAs dot structure exhibited an autocorrelation Hurst parameter of approximate 0.67 with an autocorrelation length of 90 nm and height-height difference correlation length of 56 nm. An uncapped InGaAs dot structure with two buried InGaAs dot layers exhibited an autocorrelation Hurst parameter of approximate 0.45 with an autocorrelation length of 70 nm and height-height difference correlation length of 47 nm. A 220 nm capped three layers InGaAs dot structure on the other hand exhibited an autocorrelation Hurst parameter of approximate 0.9 with an autocorrelation length of 190 nm and height-height difference correlation length of 130 nm. All samples exhibited height-height difference Hurst parameters and power spectral density Hurst parameters of 1 (indicating Gaussian distributions). All images analyzed were 10x10 µm@super 2@ in size. The analysis indicates that as more dot layers are incorporated in the structure, the fractal nature of the over layer increases. This nature is reversed by a thick capping layer. @FootnoteText@ @footnote 1@ D.B. Fenner, J. Appl. Phys., 95(10),5408-5418 (2004)@footnote 2@ K. Krishnaswami, Mater. Res. Soc. Symp. Proc. Vol.829 (2005).

AS-MoP14 Potential Difference Mapping of Molecules and Particles on Insulating Substrate, *F. Yamada, T. Matsumoto, H. Tanaka, T. Kawai,* Osaka University, Japan

A lot of research groups are challenging to fabricate molecular devices by using self-assembly of molecules. For this purpose, the knowledge of local surface potential is essential to understand and control the driving force of the self-assembly. However, it is very difficult to measure the electric properties of nano structures of the molecular devices because such devices are created on an insulating substrate. We report here surface potential measurement of DNA and nanoparticle on an insulating substrate. We used the frequency mode non-contact AFM (FM-ncAFM). NC-AFM is able to measure local electrostatic force with high sensitivity and NC-AFM prevents the charge injection induced by tip-sample contact. The measurement reveals that the potential of DNA is higher than mica and sapphire surface. In this experiment, we demonstrated that the NC-AFM enables us to obtain surface potential images of molecules on insulating substrates. We also measured the d(@DELTA@f)/dV images of DNA and Au nanoparticles on mica. We found that the plots of the d(@DELTA@f)/dV as a function of bias voltage give characteristic slopes indicating the dielectric constants of different absorbates. This result means that this measurement can be used to discriminate surface species on an insulating substrate. To discuss about the contrast mechanism of the surface potential imaging on insulating substrate, this result is beyond the understanding based on

Kelvin force microscopy because the surface potential of insulating substrate is indefinable. Then, we calculate electric filed just below the tip apex using finite element method. The calculation results reveals that the electric field just below the tip apex is enough strong to detect the local charge on surface adsorbate even if the substrate is insulator.

AS-MoP15 Surface Structure of Thermal Neutron Absorbing Ni-Cr-Mo-Gd Alloys, *P.J. Pinhero*, *T.L. Trowbridge, T.E. Lister, R.E. Mizia,* Idaho National Laboratory

A new thermal-neutron-absorbing Ni-Cr-Mo-Gd alloy was developed at the Idaho National Laboratory (INL). The purpose of this alloy is to potentially absorb neutrons liberated from spent nuclear fuel (SNF) and mitigate any issues related to nuclear criticality. The microstructure of this alloy indicates a two-phase structure consisting of the primary Ni-Cr-Mo austenite matrix phase and secondary Ni$_5$Gd phase inclusions arising from the precipitation of the austenite-insoluble Gd. Presently, this alloy is under consideration for use within the U.S. Department of Energy (DOE) standardized SNF waste packages. To support the case for this alloyâ?Ts acceptance and understand its more fundamental surface character, studies were undertaken to examine its structure and composition with respect to its bulk properties, the role of oxidation and resulting passivation on its susceptibility to corrode, and finally how these properties are influenced through boron-doping. This paper focuses on the surface structure and composition of the Ni-Cr-Mo-Gd alloy, and its boron-doped brethren, through the use of electron microscopy, electron spectroscopy, and scanning probe microscopy.

AS-MoP16 Information Needed for Improving Sputter Depth Profiling, *M.H. Engelhard*, *D.R. Baer, D.J. Gaspar,* Pacific Northwest National Laboratory

In a recent survey of needs for improving surface analysis conducted by ASTM Committee E42 on Surface Analysis, nine of the top twenty-five areas of need involved obtaining depth information. Analysts were interested in reference data, reference materials, and guides or protocols for obtaining useful information. Specific requests related to a data base containing relative sputter rates for compound materials and protocols for obtaining depth information for layered samples. Although not highlighted in the survey, accurate comparison of sputtered depths requires knowledge of the sputter rate reproducibility for a specific system before information about the relative sputter rates for different materials is meaningful. In this presentation we will present data on the reproducibility of sputter rates for our Phi Quantum 2000 and show data we have collected on the measured sputter rates for Fe$_2$O$_3$ and CeO$_2$ relative to SiO$_2$. We also note that many modern materials for which thickness information is desired are not simple thin films. We have found that apparent sputter rates for nanoporous silica films can be significantly altered (at least for a short term) by sample processing and cleaning methods.

AS-MoP17 Effect of Nitrogen on the Preparation of High Quality TiO$_{2-X}$N$_X$ Thin Films as a Photocatalyst, *K. Prabakar, T. Takahashi, **T. Nezuka**,* Toyama University, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* Yokohama City University, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Titanium dioxide (TiO$_2$) has been a well-known photocatalytic material for the past few decades, but needs UV light, so the development of a photocatalyst sensitive in visible light irradiation condition is important for indoor use. The main approaches were substitutional doping of nitrogen, since the TiO$_{2-X}$N$_X$ films absorbs visible light, we have decided to use the visible light active TiO$_{2-X}$N$_X$ film for the development of photocatalysis under controlled deposition parameters. TiO$_{2-X}$N$_X$ films were deposited on glass substrates by reactive magnetron sputtering with different Ar+O$_2$ mixture (7:3, 8:2 and 9:1) as reactive gas at different nitrogen flow ratio. Interestingly, the absorbance spectrum of the TiO$_{2-X}$N$_X$ revealed that that the amount of nitrogen doped in the TiO$_2$ films is not influenced by the nitrogen gas flow ratio but greatly depends on the sputtering pressure and substrate temperature. The properties of the films, including crystallinity, surface morphology and light absorption capability are influenced by the sputtering pressure, substrate temperature and post deposition annealing. The absorption edge shift to the visible light region and the new absorption shoulder at around 430 nm were observed for the films deposited at 0.1 Pa and annealed at 400 ° C and that they were related to the nitrogen doping, since TiO$_2$ does not absorb such visible light regions. The photocatalytic degradation of organic compounds were analyzed and discussed as a function of deposition parameters such

as gas flow ratio, substrate temperature, sputtering pressures and source to target distance. The efficiency of the photocatalytic activity of the TiO$_{2-X}$N$_X$ thin films are calculated at different light intensity, solution concentration and the results are discussed.

AS-MoP18 Sputtering Pressure Dependent Photocatalytic Properties of TiO$_2$ Thin Films, *T. Takahashi*, *K. Prabakar, T. Nezuka,* Toyama University, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* Yokohama City University, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Titanium dioxide (TiO$_2$) has been well-known as a photocatalyst. The objective of this research was to study the photocatalytic degradation of methanol and methylene blue at different light intensity and concentration by the effect of TiO$_2$ thin film deposition parameters. The TiO$_2$ films were deposited on glass substrate by direct current reactive magnetron sputtering under various total sputtering gas pressures (P$_S$) of 0.2, 0.5, 0.8 and 5 Pa and at the target to substrate distance (D$_{T-S}$) of 40 and 70 mm respectively with oxygen argon flow ratio 7:3 and 8:2 to find the optimum conditions to deposit the films with high photocatalytic activities. Structural factors dominating the photocatalytic activities were investigated in detail in relation to the sputter deposition processes. The films deposited at P$_S$ of 0.2 and 0.5 Pa and D$_{T-S}$ of 40 mm showed polycrystalline anatase structure, but, in the case of D$_{T-S}$ as 70 mm, only the film deposited at P$_S$ of 0.2 Pa showed the polycrystalline anatase structure. The films deposited at P$_S$ of 0.2 and 0.5 Pa showed decreasing tendency in the optical band gap energy and performed high photocatalytic activities. Such enhancement of the photocatalytic activity was considered to be correlated with the less number of defect level generations caused by the bombardment of the high-energy particles due to the long mean free path. The band gap energy was found to decrease from 3.4 to 3.1 eV for the TiO$_2$ films deposited at lower P$_S$ as well as the D$_{T-S}$ was 40 mm, because of the higher crystallinity compared to the films deposited at high pressures and longer D$_{T-S}$. In addition to this, the films deposited at D$_{T-S}$ of 70 mm showed the decrease in density consequently increase in the optical band gap energy. The efficiency of the TiO$_2$ catalysis was studied to evaluate the economic viability of this technique.

AS-MoP20 Development of a Plasma Process for Improving Optical and Biocompatible Properties of Contact Lens, *M. Dhayal, C.H. Kim, **C.H. So**,* Dongshin University, South Korea

The use of contact lenses is limited by its optical and biocompatible properties of materials and coatings used in the process. Therefore, a new process has been developed to improve the optical properties of contact lens materials with biocompatibilities. In this work the effect of different SiO2 and TiO2 coatings on polymeric or non polymeric material characterized for optical and biological properties. The TiO2 coatings has advantage in having low reflectance (<0.5 %) and on this coating on soft substrate materials (PMMA) can prevent from hard scratching, effect of temperature variation etc. The particular interest is in quarter wavelength thickness (100 to 200 nm) films of low reflectance for visible light wavelength (400 to 700 nm) having high optical uniformity, temperature stability, resistance to environmental and mechanical degradation. The optical properties of films (such as reflectance, refractive index) has been measured using optical spectrometer, XRD used to characterized the surface structure of films where as XPS used for surface sate analysis. Quality of composition and grain size of micro structure of coatings layer (surface) also examined using SEM, AFM.

AS-MoP21 UHV Studies of Silicon Carbide Gas Sensors with Catalytic Platinum Gates, *Y.H. Kahng*, *R.G. Tobin,* Tufts University*; R.N. Ghosh,* Michigan State University

We have studied the sensing response and surface chemistry of silicon carbide (SiC)-based gas sensors with catalytic platinum gates, in ultrahigh vacuum. Silicon carbide's large bandgap (2.4 - 3.3 eV), native oxide, and rugged physical properties make it an attractive material for use in extreme environments, including corrosive gases and temperatures up to 1000 K. Possible applications include coal burners and gasification facilities. Catalytic-gate devices based on SiC have shown response to hydrogen and hydrogen-containing gases over a wide concentration range, but details of the transduction mechanism are not fully understood. We report UHV studies of the surface chemistry and sensing behavior of prototype Pt-SiO$_2$-SiC sensors, aimed at a detailed understanding of the role of the catalytic gate in abstracting hydrogen from the analyte, providing pathways from the gate surface to the oxide interface, and catalyzing

oxidation of hydrogen desorbed from interface sites. Issues investigated include sensor response to varying partial pressures of hydrogen and oxygen and changes in gate properties resulting from gas exposure at elevated temperatures (600 - 800 K). Because sulfur is a contaminant in most fossil fuels and a notorious poison for catalysts, effects of sulfur contamination have also been studied.

AS-MoP22 Electrochemical Spectroscopic Studies of New Materials for PEM Fuel Cells, *P.C. Wong*, *D. Susac, L. Zhu, A. Sode, M. Teo, D. Bizzotto, R. Parsons, K.A.R. Mitchell,* University of British Columbia, Canada*; S.A. Campbell,* Ballard Power Systems, Canada

A new approach for designing potential catalysts for proton exchange membrane (PEM) fuel cells involves characterizing surfaces of thin film materials fabricated as possible cathodes, to avoid the expense and slow oxygen reduction kinetics associated with platinum. This paper will describe studies, especially with X-ray photoelectron spectroscopy (XPS) and scanning Auger microscopy (SAM) of metal chalcogenide surfaces before and after electrochemical activity. Particular examples will be presented for thin films formed by cobalt and selenium, and the electrochemical behaviors will be related to the surface character of the different samples.

Applied Surface Science
Room 206 - Session AS+BI-TuM

Surface Characterization of Organic and Biological Systems
Moderator: R.T. Haasch, University of Illinois

8:20am AS+BI-TuM1 Synthesis and Characterization of Mixed Polymer Brush Films, *D.J. Dyer, J. Feng,* Southern Illinois University; *R.T. Haasch,* University of Illinois-Urbana Champaign; *V.-N. Wong,* Southern Illinois University **INVITED**

Chameleons respond to their environment by changing color so that they take on the characteristics of their surroundings. Smart organic films may also respond to environmental perturbations and adapt to their environment. In particular, polymer brush films have shown remarkable switching properties, especially when the films are within the ultra-thin region from 1-100 nm. These so-called polymer brushes are composed of polymers that are tethered to an inorganic substrate and may stretch out away from that substrate. Polymer brushes that are composed of more than one component are referred to as mixed, or binary brushes. Typically, the two different polymers are randomly distributed on the surface and exhibit phase-separation and interfacial morphology that is distinct from that of spin-cast blends of the same composition. This occurs because the brush chains are confined to the substrate and are forced into contact with nearby incompatible chains, whereas in a blend the polymer chains can more easily rearrange during annealing. Here we discuss the synthesis and characterization of mixed polymer brushes on silicon and gold substrates. One of the major challenges we face is the quantification of the bulk film composition as compared to the air/liquid interface. For this we use a tandem XPS/RAIRS strategy. Our paper will place an emphasis on amphiphilic systems where one polymer is hydrophilic and the other is hydrophobic. These results demonstrate that a mixed brush of polystyrene (PS) and polyacrylamide (PAAM) may switch from hydrophobic to hydrophilic in one minute at room temperature. Such rapid switching is highly unusual for mixed brushes.

9:00am AS+BI-TuM3 Characterization of a Chemically Passivated GaAs Based Sensor Device in Air and Electrolytes, *S.M. Luber,* Walter Schottky Institut, TU Muenchen, Germany; *D. Gassull,* TU Muenchen, Germany; *D. Schuh,* Universitaet Regensburg, Germany; *M. Tanaka,* TU Muenchen, Germany; *M. Tornow, G. Abstreiter,* Walter Schottky Institut, TU Muenchen, Germany

Functionalized field effect devices are promising candidates to act as smart substrates for sensor applications. For a use in biological systems a functional layer has to provide stability against electrochemical decomposition, and allow effective coupling of the surface potential to the conductive channel. We present a resistor device passivated with a 4'-substituted 4-mercaptobiphenyl (MBP) self-assembled monolayer (SAM) for sensing applications. Base material is a GaAs-AlGaAs heterostructure containing a quasi 2D electron gas 60nm beneath the surface. In the first part of our study we investigated the influence of the MBP-SAM on the electronic surface properties of n-doped GaAs samples employing the Kelvin probe technique. We changed the dipole moment of the MBP molecules using various substituents (-H, -OH, -CH$_3$) and found a linear effect on the electron affinity. In the second part we tested the stability of the resistor device based on the GaAs-AlGaAs heterostructure in aqueous solutions. Whereas a bare device degraded rapidly the coated samples showed a remarkable increase in stability. Furthermore we characterized samples coated with monolayers with CH$_3$ (MBP-CH$_3$) and OH (MBP-OH) substituents in buffered electrolyte solutions with varying pH. For the MBP-OH coated sample, a change in pH induced a change in the resistance of the device. Interestingly, the sample grafted with an MBP-CH$_3$ SAM also showed a clear response on pH which can be attributed to the adsorption of OH$^-$ ions on CH$_3$ groups.

9:20am AS+BI-TuM4 Ion Beam Alignment of Nematic Liquid Crystal on PPV-layer, *S. Pylypenko, K. Artyushkova, J.E. Fulghum,* The University of New Mexico; *O. Buluy, T. Prokopenko, Y. Reznikov,* Institute of Physics of National Academy of Sciences, Ukraine

The development of LCD technologies requires homogeneous alignment of liquid crystals (LCs). The traditional rubbing procedure, consisting of unidirectional brushing of the aligning substrates, is quite reliable but has some drawbacks, including the production of electrostatic charges and dust during the rubbing. Ion and plasma-beam alignment are among the more promising candidates to replace the rubbing procedure. Ion beam alignment is based on an angularly selective destruction and

rearrangement of the surface material as a result of ion bombardment, creating orientational order on the initially isotropic surface. Here we report on effective alignment of LCs on an ion-bombarded PPV layer. Glass substrates covered with a thin layer of PPV were irradiated using 2KeV Ar$^+$ ions for varying times. The irradiated substrates were used to assemble planar cells, and the gap was filled with nematic LC 5CB. The measured value of the anchoring energy of ~ 3 10^{-3} erg cm-2 appeared to be one to two orders of magnitude less than the typical value produced by plasma/ion-alignment. We found enhancement of the stability of the PPV layer in the irradiated area. The strong interaction of 5CB molecules with the PPV surface caused dissolution of the PPV by the LC, and the PPV-layer was not affected by LC in the irradiated region. Three-dimensional characterization of the polymer by X-ray Photoelectron spectroscopy (XPS), Angle Resolved XPS (ARXPS), and Confocal Microscopy (CM) utilizing multivariate analysis (MVA) techniques were carried out to study the mechanism of PPV alignment after ion-beam bombardment. Our results demonstrate that ion-beam treatment provides uniform alignment of liquid crystals characterized by a weak anchoring.

9:40am AS+BI-TuM5 Plasma Beam Alignment for Liquid-Crystal Displays, *Y.-F. Chang, C.-H. Lin, C.-W. Chen,* Industrial Technology Research Institute, Taiwan

Surface alignment of liquid crystals is an important issue in practical applications of liquid crystal (LC) cells on TFT-LCD process. The most common technique of LC alignment is an unidirectional rubbing on special polymer films which deposited on an conductive substrate such as ITO (Indium-Tin Oxide). The rubbing process has many disadvantages even though it has been widely used in the actual production of LCD. Thus, rub-free methods for LC alignment are strongly required in the next generation LCD technology. A number of non-contact LC alignment methods have been proposed in attempting to replace the rubbing process. And the well-known technique is ion beam irradiation proposed by IBM group. Another non-mechanical alignment technique, named photoalignment method, in which the UV light irradiation caused surface anisotropy of the bounding plates was studied for many years. The method was relatively simple, but the corresponding drawbacks such as weak anchoring energy as well as poor photo and thermal stability, may limit the application of this technology. In this research, a plasma beam alignment technique, in which the aligning substrate was treated with a flux of plasma that was extracted and accelerated electrostatically, was applied on the PI and diamond-like carbon (DLC) film. It is also a non-contact alignment process. The plasma flux was generated with a DC plasma source known as the anode layer thruster (ALT). The discharge channel was used to produce the sheet-like fluxes. The test panels (100 mm X 50mm) were fabricated with various plasma-beam processing parameters, w/o further passivation processes to study the alignment qualities including the pretilt angle, anchoring energy, VHR and Rdc as a function of these processing parameters. In addition, the measuring methods of these alignment qualities were also investigated in this study.

10:00am AS+BI-TuM6 Measuring the Thickness of Organic/Polymer/Bio Films on Glass Substrates using Spectroscopic Ellipsometry, *H.G. Tompkins, T. Tiwald, C. Bungay,* J. A. Woollam Co., Inc.; *A.E. Hooper,* Motorola, Inc.

In this work we discuss a method of determining film thickness for film/substrate combination where the index of refraction of the film and substrate in the transparent spectral regions are almost identical. Common examples of this situation are organic/polymer/biological films on glass substrates. IR ellipsometry is used and we use weight gain to provide some necessary additional information for determining the optical functions for the film material. The spectral regions of strong molecular vibrations are then used for determining film thickness.

10:20am AS+BI-TuM7 Applications of Surface Analysis in the Medical Device Industry, *A.M. Belu,* Medtronic, Inc.

The surface is an important zone as it is the interface between a material of interest and the environment with which it interacts. For biomaterials and drug delivery systems, knowledge of interface chemistry is important for understanding how a material will interact with the biological environment of the body. For other materials, particularly those that are employed in the manufacture of medical devices, evaluation of the surface is important to further understand issues with welding, adhesion, contamination, discoloration, etc. This talk will highlight the power of surface analysis methods and how they are employed in the medical device industry. The analytical methods include TOF-SIMS and ESCA which allow chemical characterization of the uppermost ~75Å of a material. Scanning probe

microscopy (SPM) and laser profilometry are used to gain topographical information and to measure roughness of surfaces. A field emission scanning electron microscope (FE-SEM) allows high resolution imaging of surfaces with resolution capabilities to 1 nanometer. A low vacuum SEM further allows characterization of non-conductive, wet, and organic samples. SEM also has the capabilities for elemental identification and semi-quantitative analysis using an x-ray detector (EDS). Examples will be presented to demonstrate a range of surface analysis applications, from fundamental studies of biomaterials, to solving industrial problems. The power as well as the problems of data acquisition and interpretation will be highlighted with regards to each technique. Further, a comparison of all techniques will be made to help elucidate which method or methods are best for specific problems. Examples will include imaging the distribution of drug in a polymer coating (such as on stents), identifying contamination on medical devices (such as detergent residue on leads), evaluation of particles and defects, and characterization of surface chemical modification.

10:40am AS+BI-TuM8 Microelectronic Multielectrode Interface for Evaluation of Living Cells, *H.D. Wanzenboeck*, P. Hagl, K. Dominizi, E. Bertagnolli, Vienna University of Technology, Austria; E. Bogner, M. Wirth, F. Gabor, University Vienna, Austria

*****PLEASE NOTE: YOU MUST IDENTIFY A DIFFERENT PRESENTER FOR THIS ABSTRACT. YOU MAY ONLY PRESENT ONE (1) PAPER AT THE CONFERENCE.*****Tests on living cells are crucial in biomedical research, biotechnology , pharmacological diagnostics and medicine, but applied methods are often labor-intensive. Microelectronic technology has available sensitive techniques for automatized, continuous measurement and data interpretation. These advantages are not made use of due to the complex nature of the interface between the biological and microelectronic world. This work describes the fabrication and fundamental application of a functionalized biomaterial interface. For an interface to biological substances the choice of suitable substrate materials is decisive. A biological layer of human ephitelial cells (Caco-2) was grown in-vitro on the interface. The biocompatibility of inorganic and organic materials typically used in microelectronics was exploited. Metals, dielectrics and semiconductors were evaluated qualitatively by optical imaging and by scanning electron microscopy at variable pressure. A quantitative evaluation was performed with biochemical tests on cell proliferation and differentiation. Fundamental aspects of bio-interface engineering are investigated by interface analysis methods. In a second step 3-dimensionally patterned surfaces were explored as interface to the biological world. By microstructuring a miniaturisation of typical structures in the range of 20 μm down to 1 μm - smaller than the diameter of a living Caco2 cell - was performed. A functional microelectrode array proved to be an excellent bio-interface to living cells. The growth and behaviour of a Caco-2 cell layer on this array of multiple microelectrodes was studied by optical and electrical measurements. The electrical measurement through a single Caco-2 cell was recorded as impedance spectrum. The results contribute to the further understanding of the interactions between living cells and microelectronic biosensors. This work provides fundamentals to unite microelectronic engineering with in-vitro biological studies.

11:00am AS+BI-TuM9 Chemical Imaging of Biological Cells and Tissues using TOF-SIMS, *P. Sjovall*, SP Swedish National Testing and Research Institute, Sweden   **INVITED**

Although time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been used for chemical imaging of cells and tissues for almost 10 years, recent advances (notably the new primary cluster ion sources) have the potential to lead to a new breakthrough in this area. To realize this, however, additional research is required, addressing issues like (i) sample integrity, (ii) lateral resolution / detection efficiency, and (iii) sample complexity. We have used TOF-SIMS to record the spatial distribution of lipids in freeze-dried mouse brain sections and in surface-adhering polymorphonuclear leukocytes (PMNLs). The mouse brain sections (14 μm thick, cryosectioned, placed on a glass or Si substrate and freeze-dried inside the TOF-SIMS instrument or in a separate vacuum chamber) were analyzed using Au@sub n@@super +@ and Bi@sub n@@super +@ primary ions. It is demonstrated that TOF-SIMS analysis can provide detailed images showing the distribution of a number of lipids on the tissue surface at lateral resolutions down to < 1 μm.@footnote 1@ It is also shown that migration of lipids may be a problem under certain sample preparation and analysis conditions. The PMNLs were analyzed using a chemical imprinting technique, in which the outermost molecular layers of the cells are transferred to a substrate surface by pressing the substrate against the cell sample. The advantage of this method is that the substrate

surface can be selected and/or functionalized in a manner that optimizes the subsequent imaging TOF-SIMS analysis. For the PMNLs, chemical imprints were made on Ag substrates in order to improve the detection yield and specificity of the lipids using Ga@super +@ primary ions (taking advantage of the Ag cationization). The resulting images show a complementary localization of cholesterol (plasma membrane) and phosphocholine (nuclear membrane).@footnote 2@ @FootnoteText@ @footnote 1@ Anal. Chem. 2004, 76, 4271@footnote 2@ Anal. Chem. 2003, 75, 3429.

11:40am AS+BI-TuM11 Studying the Effect of Spacer Thiol Chemistry, Orientation and Surface Coverage on the Hybridization Properties of Mixed DNA SAMs on Gold, *C.-Y. Lee*, University of Washington; P. Gong, Colorado State University; H.E. Canavan, L.J. Gamble, University of Washington; D.W. Grainger, Colorado State University; D.G. Castner, University of Washington

Although it is desirable to capture DNA targets without purification from complex milieu (e.g., serum, tissue lysate) for microarray applications, this goal is often hindered by non-specific attachment of DNA and proteins. Minimizing nonspecific adsorption to biosensors and microarrays requires a non-fouling background. Furthermore, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. To achieve each of these goals, we evaluated the effect that two spacer thiols [11-mercapto-1-undecanol (MCU) and 11-mercapto-undecyl tetra ethylene glycol (OEG)] have on surfaces prepared using singled-stranded DNA containing a thiol anchor group (SH-ssDNA). These mixed DNA self-assembled monolayers (SAMs) have been studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure spectroscopy (NEXAFS), @super 32@P-radiolabeling, and surface plasmon resonance (SPR). Although XPS and radiolabeling indicate that SH-ssDNA surface coverage steadily decreases with longer exposure to the backfill molecules, NEXAFS indicates that polarization dependence peaks at short MCU and OEG exposure times (< 1h), after which polarization dependence decreases due to the loss of DNA from the surface. A comparison of hybridization responses from these probe surfaces was made using SPR by exposing the surfaces to complementary DNA in various concentrations of serum. SPR results indicate that although surfaces with MCU and OEG thiol spacers showed resistance towards non-specific DNA binding in pure buffer, hybridization efficiency is hindered by non-specific serum protein adsorption even at minimal serum concentration of 1%. Finally, differences in the hybridization property and protein resistance of the SH-ssDNA/MCU and SH-ssDNA/OEG mixed monolayer surfaces will be discussed.

Applied Surface Science
Room 206 - Session AS-WeM

Essential Tools for Surface Analysis
Moderator: J.E. Fulghum, University of New Mexico

8:20am AS-WeM1 TOF-SIMS: Accurate Mass Scale Calibration, *F.M. Green, **I.S. Gilmore**,* National Physical Laboratory, UK*; M.P. Seah,* National Physical Laboratory, UK, United Kingdom
A study is presented of the factors affecting the calibration of the mass scale for TOF-SIMS. At the present time, analysts achieve a mass accuracy of only 150 ppm for large molecules (647 amu) and for smaller fragments of < 200 amu may typically be 60 ppm. The instrumental stability is 1 ppm and better than 10 ppm is necessary for unique identification of species. In the recent interlaboratory study@footnote 1@ only 3 instruments out of 32 were within 10 ppm for smaller fragments. The experimental uncertainty can lead to unnecessary confusion where peaks are wrongly identified or are ambiguous. Here we study in detail the instrumental parameters of a popular reflection TOF-SIMS. The effect of the ion kinetic energy, emission angle and other physical and instrumental operating parameters on the measured peak position are determined. This clearly shows why molecular and atomic ions have different mass accuracy and peak shapes. These data provide the basis for a coherent procedure for optimising the instrumental settings for accurate mass calibration and rules by which inorganics and organics may be incorporated. This leads to generic sets of ions for mass calibration, which, used for re-calibration, improves the mass accuracy of the interlaboratory study data@footnote 1@ by up to a factor of 4. Now, 12 instruments out of 32 are within the 10 ppm range. The effects of extrapolation beyond the calibration range are discussed and a recommended procedure given to ensure that accurate mass of large molecules is achieved within a selected uncertainty. One bonus of this study is that the instrument can now be operated in a regime with good energy discrimination to study the fragmented energies of molecules. We shall discuss how this compares with data from G-SIMS@footnote 2@ and supports the G-SIMS concept. @FootnoteText@ @footnote 1@ I S Gilmore, M P Seah and F M Green, submitted Surf. Interface Anal.@footnote 2@ I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000), p. 465.

8:40am AS-WeM2 Quantitative XPS: Quadrupole Terms, Shake-Up, Shirley Background and Relative Sensitivity Factors, *M.P. Seah,* National Physical Laboratory, UK, United Kingdom*; I.S. Gilmore,* National Physical Laboratory, UK
An analysis is provided of the XPS intensities measured in the NPL XPS database for 46 solid elements. This present analysis does not change the previous conclusions concerning the excellent correlation between experimental intensities following deconvolution using the angle-averaged REELS data and the theoretical intensities involving the dipole approximation and Scofield's cross sections. Here, we test the more recent calculations for cross sections by Trzhaskovskaya et al with quadrupole terms and find that their cross sections diverge from the database by up to a factor of 2. The quadrupole angular terms lead to small corrections also evaluated in the present analysis. Measurements of the extent of shake-up for the 46 elements broadly agree with theoretical calculations but details of the observed element-to-element variation are not reproduced in those calculations. The predicted theoretical constancy in the shake-up contribution implies that the use of the Shirley background will lead to a peak area that is a constant fraction of the true peak area including the shake-up intensities. If this were the case, the peak areas using the Shirley background would be a valid measure of intensity. We would therefore expect that the ratio of the peak area using the Shirley background to the intensity calculated using the cross sections, etc, would be a constant value, less than unity, with a reasonably small scatter. Unfortunately, the variability of the shake-up contribution, and the variability with which the Shirley background reproduces the angle-averaged background under the peak, itself, both combine to leave a 38% relative standard deviation in this ratio. The Shirley background thus appears to be a poor method for general quantitative analysis. Its use may need to be limited to specific situations where the sensitivity factors have been obtained from reference samples similar to those being analysed.

9:00am AS-WeM3 SURFACE SCIENCE SPECTRA: The AVS Surface Science Database for the Surface Spectroscopy Community, *S.W. Gaarenstroom,* General Motors R&D Center   **INVITED**
The surface spectroscopy community shares high-quality spectral data on hundreds of materials by means of the AVS Surface Science Database. Most of the shared spectral data is obtained by x-ray photoelectron spectroscopy, but Auger electron spectroscopy, secondary ion mass spectrometry, electron energy loss spectroscopy and other techniques are also represented. This database effort, named SURFACE SCIENCE SPECTRA, was launched in 1992. The SSS developers benchmarked and built upon the database efforts made for other kinds of spectroscopies (such as infrared spectroscopy, mass spectrometry, and x-ray diffraction), but were also attentive to the special needs in the surface science community. The contributors to the spectral database are from the worldwide surface science community at large (more than 450 individual contributors from more than 110 different institutions). The evaluators of the database are also from the entire surface science community, because all data records are peer-reviewed prior to acceptance and entry into the database. Simultaneous with the launch of the journal product of the SURFACE SCIENCE SPECTRA database, massive changes began in the publishing world's electronic technology and the individual scientist's preferences for accessing information. While the descriptors in each individual data record have changed only minimally in the years since the database launch, the delivery mechanism changed continually and will continue to change. The current conversion of the on-line journal to XML publishing technology provides new opportunities to inexpensively add useful features for the benefit of the database users.

9:40am AS-WeM5 Software Package to Determine @epsilon@(k,@omega@) from Analysis of REELS, *S. Tougaard,* University of Southern Denmark, Denmark*; F. Yubero,* Inst. de Ciencia de Materiales de Sevilla, Spain
Engineering of new thin solid films of varying composition are of current high technological interest. Methods to determine the electronic properties of thin films are therefore of increasing importance. The complex dielectric function @epsilon@(k,@omega@) contains valuable information on the electronic structure. The effective single scattering cross section can be determined from analysis of reflected electron energy loss spectra (REELS)@footnote 1@ and a semi-classical dielectric response model for REELS was also developed.@footnote 2,3@ It has been shown how this can be applied to determine @epsilon@(k,@omega@) from analysis of experimental REELS. This provides an intesting technique because REELS is rather simple to apply, it is inexpensive, it is available in many laboratories and above all it can easily be applied to thin films of only a few nano-meters thickness grown on a supporting substrate. The complexity of the formulas has however been a hindrance for widespread use of the technique. To make it generally available, we decided to develop a software package with a user friendly graphical interface and interactive facilities. We hope that this tool will inspire more widespread use of this method to explore the electronic properties of solids and thin films. @epsilon@(k,@omega@) can also be used to make quantitative interpretation of the fundamental mechanisms in photo- and Auger electron spectroscopy and to calculate the inelastic mean free path for electrons in solids and determine the excitations that take place when the electron moves in the surface region or in the vacuum above the surface. The software, which is free of charge for non-commercial use, handles the theory developed in the following papers:. @FootnoteText@ @footnote 1@ S. Tougaard and I. Chorkendorff, Phys. Rev. B23 6570 (1987)@footnote 2@ F. Yubero and S. Tougaard, Phys. Rev B46, p. 2486 (1992)@footnote 3@ F. Yubero, J.M. Sanz, B. Ramskov and S. Tougaard, Phys Rev. B53, 9719 (1996).

10:00am AS-WeM6 Complete Analysis of ToF-SIMS Spectral Images in a Research and Development Analytical Laboratory, *V. Smentkowski,* General Electric Global Research Center*; M. Keenan, J.A. Ohlhausen, P.G. Kotula,* Sandia National Laboratories
Time of flight secondary ion mass spectrometry (ToF-SIMS) spectral image raw data files contain a wealth of information since an entire mass spectrum is saved at each pixel in an ion image. Currently, few tools are available to assist the analyst in visualizing the entire raw data set and as a result, most of the measured data are never analyzed. Typically, the ToF-SIMS analyst manually selects a few species to monitor based upon input from the customer, knowledge of results obtained from similar past analysis, high peak intensity and/or unusual species detected in the spectrum. Manual analysis is complicated by the fact that little is known about real-life samples prior to analysis. The analyst is expected to perform rapid, cost effective, analysis and provide a complete description of the sample. Automated, non-biased, multivariate statistical analysis (MVSA) techniques are useful for converting the massive amount of data into a smaller number of components that are needed to fully describe the ToF-SIMS measurement. We are using AXSIA to perform MVSA on ToF-SIMS

raw data files. The advantages of AXSIA include: the ability to select the mass range of interest, the ability to bin the mass spectra from 0.001amu to 1amu, optimal scaling of the data to account for Poisson counting statistics, and the generation of intuitive results. Examples will be selected to demonstrate these advantages. We will also demonstrate that positive ion and negative ion raw data files collected on the same region of a sample can be concatenated. MVSA analysis of the concatenated data provides a complete description of the sample. The analytical insight provided by concatenated MVSA analysis would be difficult, if not impossible, to obtain via other routes. Sandia National Laboratories 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.

10:20am **AS-WeM7 Principal Components Analysis of TOF-SIMS Data: Why, What, and How**, *D.J. Graham,* University of Washington **INVITED**
Even the simplest TOF-SIMS spectrum can be complex. A typical spectrum may contain hundreds of peaks, the intensities of which can be correlated. This complexity has led to the exploration and application of multivariate analysis (MVA) methods to TOF-SIMS data in an attempt to simplify analysis and maximize the information content extracted from the data. MVA of TOF-SIMS spectra has shown promise and success for spectra and images across many systems including self-assembled monolayers, proteins, and polymers. Due to this success, multivariate analysis of TOF-SIMS data is quickly becoming more standard within the surface analysis community, yet there have been no standards set regarding how to properly apply multivariate methods to TOF-SIMS data. It is important to make sure that as progress continues in the application of MVA methods to TOF-SIMS data, standards be established in the application of theses methods, and that effort be made in the optimization of these methods, and the education of the community. This talk will highlight important considerations in the use of PCA with TOF-SIMS data. Experimental design, peak selection, data preprocessing and data interpretation will be discussed as it pertains to PCA of TOF-SIMS spectra.

11:00am **AS-WeM9 Automated Peak Identification in a TOF-SIMS Spectrum**, *H. Chen,* E.R. Tracy, W.E. Cooke, M.W. Trosset, College of William and Mary; *D. Malyarenko,* INCOGEN Inc.; *D.M. Manos,* College of William and Mary; *M. Sasinowski,* INCOGEN Inc.
Although the high mass resolution, imaging capability and the high-throughput capability of mass fingerprint measurements have made TOF-SIMS one of the standard tools for research in surface analysis. A bottleneck is that TOF-SIMS produces very large raw data sets that must be preprocessed to identify the mass peaks for further analysis, especially when complex biological samples produce a large number of peaks. The accuracy of the mass assignment, which is critical when comparing mass fingerprints with databases, can be another limitation. Under survey conditions, the positions of the desired mass peaks are commonly not known beforehand, and TOF-SIMS peak-picking requires a procedure to distinguish mass peaks from background noise. Often, those peaks and their positions are identified manually. This introduces a subjective error due to the asymmetric peak line shape and to Poisson (counting) noise which has larger variance at larger peaks. This results in a degradation of the apparent machine performance and an inconsistency in the peak identification. We have developed an automated peak picking algorithm based on a maximum likelihood approach that effectively and efficiently detects peaks in a TOF-SIMS spectrum. The algorithm takes into account the underlying characteristic Poisson process and asymmetric peak line shape and produces maximum likelihood estimates of peak positions and amplitudes. It also simultaneously develops estimates of the uncertainties in each of these quantities. With this approach, we avoid the ambiguities involved in manual peak picking and mass assignments. We use the estimated peak positions, amplitudes and their uncertainties to align different spectra more accurately than is possible by using a few known calibrants. This precise peak summary is crucial for further multivariate analysis.

11:20am **AS-WeM10 More Information from Shorter Acquisition Times in XPS Imaging and Other Multivariate Surface Analytical Datasets**, *P.J. Cumpson,* National Physical Laboratory, UK
Quantification of multivariate datasets, such as XPS images, is a major area of research due to the impressive capability of modern instruments. It can, however, present challenges in terms of signal-to-noise and long acquisition times. A very simple but computationally-intensive Bayesian chemometric method@footnote 2@ for addressing this problem was published around ten years ago. With increasing personal computer speeds

this has become not just more practical, but even very rapid today. This approach to electron counting statistics results in a novel quantification method that halves acquisition time, or equivalently, results in an increase in signal-to-noise of roughly a factor of 1.4, rising to 1.7 for the shortest acquisition time, noisiest images. This is not a ``black box'' statistical method, but a relatively simple way of building-in the assumption that the primary beam is fairly stable from pixel-to-pixel, which is certainly the case for modern XPS instruments. The method is potentially valuable in depth-profiling too. We show that combining this method with rapid Monte Carlo methods@footnote 3,4@ (whose routine use has also become much more practical recently) leads to several important new chemometric methods for count-limited, multivariate surface analytical data in general. @FootnoteText@ @footnote 1@ K Artyushkova and J E Fulghum in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Ed. D Briggs and J T Grant (IM Publications, Chichester UK, 2004).@footnote 2@ P J Cumpson and M P Seah, Surface and Interface Analysis, 18 (1992) 361.@footnote 3@ P J Cumpson, Surface and Interface Analysis 20 (1993) 727.@footnote 4@ D Ze-jun and R Shimizu in "Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", Ed. D Briggs and J T Grant (IM Publications, Chichester UK, 2004). .

11:40am **AS-WeM11 Improvements in the Spatial and Spectral Resolution of X-ray Photoelectron Images through Multivariate Analysis and Multisensor Fusion**, *K. Artyushkova, J.E. Fulghum, L.R. Williams,* The University of New Mexico; *S.J. Hutton, S.J. Coultas,* Kratos Analytical Ltd., UK
Improvements in spectral and spatial resolution of imaging X-ray photoelectron data are of growing importance, as the chemical complexity of materials under study increases, and the size of features to be resolved decreases. In this work we use a combination of multivariate analysis methods (MVA) and multisensor image fusion to resolve photoelectron image features in components that are similar in chemistry and small in size, relative to the spatial resolution of the technique. Methods combining XPS image acquisition schemes with multivariate analysis were tested to facilitate analysis of multicomponent samples containing spectrally overlapped chemical components. Additional spatial distribution information can potentially by obtained through multisensor image fusion of atomic force microscopy (AFM) and XPS images. X-ray photoelectron spectroscopy (XPS) has a high energy resolution but relatively low spatial resolution. In contrast, AFM images have significantly higher spatial resolution. We report initial efforts to combine low resolution color images (XPS) and a high resolution monochromatic images (AFM) to produce a higher spatial resolution XPS images. The validity of these approaches will be demonstrated using patterned SAM samples with known chemistry and spatial morphology. Application of these methods will be shown using images from phase-separated polymer blends. This work has been partially supported by NSF CHE-0350666 and UNM.

Applied Surface Science
Room 206 - Session AS-WeA

SIMS Cluster Probe Beams and General Topics
Moderator: I.S. Gilmore, National Physical Laboratory, Australia

2:00pm AS-WeA1 Analysis of a Model System for Reactions of Organic Molecules on Atmospheric Particles: SAMS and Ozone, *D.J. Gaspar,* Pacific Northwest National Laboratory*; T.M. McIntire,* University of California, Irvine*; A.S. Lea, N. Jaitly,* Pacific Northwest National Laboratory*; Y. Dubowski,* Technion-Israel Institute of Technology*; B.J. Finlayson-Pitts,* University of California, Irvine

Self-assembled monolayers (SAMS) provide a useful model system for the study of reactions of organic molecules. The preparation, use and analysis of SAMS are prone to variability and artifacts that can confound measurements that are do not provide molecular information on the state of the surface. Time of flight secondary ion mass spectrometry, on the other hand, provides a direct probe of the SAM surface chemistry. In this work, we describe our efforts to extract useful information regarding the reaction of ozone with saturated and unsaturated organic monolayers covalently bound to silicon dioxide surfaces under atmospherically relevant conditions. We have used a combination of imaging TOF-SIMS and spectral analysis aided by principal component analysis (PCA) to extract chemical information about the reaction of two model SAMS with ozone. The TOF-SIMS data provide the molecular information necessary to accurately interpret data obtained using other methods and described herein, including atomic force microscopy (AFM), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning Auger microscopy (AES). We show that the organic monolayer is removed from the Si substrate by ozone for an unsaturated 1-octene (C8=) monolayer, while it remains intact for a saturated dodecane (C12) monolayer. The implications of these observations for the atmospheric chemistry of organic molecules are discussed.

2:20pm AS-WeA2 Formation and Volatilization of Small Molecules From a PTFE Matrix Upon MeV Alpha Particle Irradiation Examined by ToF-SIMS, SEM, and RGA, *G.L. Fisher,* R.E. Lakis, C.C. Davis, C.J. Wetteland, Los Alamos National Laboratory*; C.W. Szakal, N. Winograd,* Pennsylvania State University

The chemical structure and morphology at the surface of @alpha@-irradiated polytetrafluoroethylene (PTFE) has been examined and compared to unirradiated PTFE. The samples were irradiated to doses of 10^7 to 10^{11} Rad using 5.5 MeV [^{4}He]$^{2+}$ from a tandem accelerator beam line. Static time-of-flight SIMS (ToF-SIMS), using a 20 keV C$_{60}^+$ source, was employed to probe chemical changes versus irradiation. Chemical images and high resolution spectra in both positive and negative polarity were collected and analyzed to reveal the effects of @alpha@ particle radiation on the chemical structure. Where appropriate, comparison is made to static ToF-SIMS data collected using a 15 keV Ga$^+$ primary ion source. Residual gas analysis (RGA) was utilized to monitor the evolution of volatile species during vacuum irradiation of the samples. Secondary electron microscopy (SEM) was used to observe the morphological variation of samples with increasing @alpha@ particle dose. The data show that PTFE nominally retains its chemical structure and morphology at @alpha@ doses @<=@10^9 Rad; however, at @alpha@ doses @>=@10^{10} Rad the PTFE matrix suffers severe chemical degradation, morphological roughening, and material loss. Chemical degradation is evidenced in the ToF-SIMS spectra by fragmentation, unsaturation, and speciation of molecules in the PTFE matrix. ToF-SIMS images support the assertion that chemical degradation is the result of @alpha@ particle irradiation and show morphological roughening of the sample with increased @alpha@ dose. High resolution SEM images more clearly illustrate morphological roughening and the mass loss that accompanies high doses of @alpha@ particles. Finally, RGA confirms the supposition that the product of chemical degradation in the PTFE matrix with continuing irradiation is evolution of volatile species resulting in morphological roughening and mass loss.

2:40pm AS-WeA3 Depth Profiling Analysis by Secondary Ion Mass Spectrometry: Historical Perspective and Current State-of-the-Art, *C.W. Magee,* Evans East **INVITED**

Secondary ion mass spectrometry has been used for in-depth characterization of materials and process for over 30 years. This talk will first touch briefly on history of SIMS depth profiling and then will review current state-of-the-art examples in semiconductors materials as well as in

other areas as diverse from IC chips as potato chip bags and, yes, even the kitchen sink. Semiconductor areas will include, among others: profiling of ion implants with energies of a few hundred eV to a few million eV, along with high precision dose determination; and analyses of dopants and matrix elements in areas only a few 10's of um@super 2@. In addition, the talk will illustrate the utility of backside polishing for sample preparation.

3:20pm AS-WeA5 SIMS Depth Profiling of Deuterium Labeled Polymers in Polymer Films and Multilayers, *S.E. Harton,* F.A. Stevie, D.P. Griffis, H. Ade, North Carolina State University

Thin planar polymer films are model systems for probing physical phenomena related to molecular confinement at polymer surfaces and polymer-polymer interfaces. Secondary Ion Mass Spectrometry (SIMS) can provide real-space depth profiles of tracer labeled polymers directly with sufficient depth resolution for optimal analysis of these systems. Three different bilayer systems have been used to investigate various physical phenomena at polymer-polymer interfaces, including reactive compatibilization and interfacial segregation. Deuterated polystyrene (dPS) has been employed as the tracer polymer and has been imbedded in a matrix of either unlabeled polystyrene (PS) or poly(cyclohexyl methacrylate) (PCHMA). Using selective solvents and a direct casting method, these doped films have been placed on either poly(methyl methacrylate) (PMMA) or poly(2-vinyl pyridine) (P2VP) and thermally annealed. X-ray specular reflectivity measurements confirm ultra-sharp interfaces between the two polymers using this preparation method, allowing for maximum depth resolution during SIMS analysis. Varied analysis conditions for a magnetic sector instrument (CAMECA IMS-6f) were used to optimize the depth resolution and sensitivity while minimizing matrix effects and sample charging. For all systems Cs+ and O2+ have been used as the primary ion source, with detection of negative and positive secondary ions, respectively. Impact energy and primary ion species have been shown to affect matrix ion count rate for the various films studied. Conditions required to achieve constant matrix secondary ion yield across the heterogeneous interface are discussed.

3:40pm AS-WeA6 Adjacent Electron Beam Method for SIMS Analysis of Insulators at High Depth Resolution Conditions Using a Magnetic Sector Instrument, *C. Gu, Z. Zhu,* **F.A. Stevie,** *D.P. Griffis,* North Carolina State University

The adjacent electron beam charge neutralization method@footnote 1@ provides sufficient and self regulating charge neutralization for positive secondary ion SIMS analysis of both bulk and thick layer insulators using a magnetic sector instrument. This charge neutralization method has been extended to low primary ion impact energies, thus providing the ability to obtain high depth resolution SIMS analysis of both bulk and thick film insulating materials at high mass resolution. Results have been achieved with O$_2^+$ impact energy of 1.25keV and electron impact energy of 2.75keV. All prior analyses had been made using 5.5keV for O$_2^+$ and 6.5keV electron energy. Charge neutralization has been achieved for SiO$_2$, AlN, and AlGaN samples. Profiles have been obtained through at least two micrometers of insulator under the low impact energy conditions. While being able to profile through thick films is important, the real significance in these results is the ability to provide high depth resolution SIMS analysis of insulating materials. Electron impact charge neutralization using the adjacent electron beam method has been achieved with the following metal coatings: Al, Au, Ru, and Ir. Results will be presented demonstrating this method for both bulk and thick film insulating materials and current understanding of the mechanisms involved in this method of self regulating charge neutralization will be discussed. @FootnoteText@ @footnote 1@ A. L. Pivovarov, F. A. Stevie, and D. P. Griffis, SIMS XIV Proceedings, Applied Surface Science 231-232, 786-790 (2004).

4:00pm AS-WeA7 The Atomic Motions behind Cluster Bombardment Secondary Ion Mass Spectrometry, *B.J. Garrison,* Penn State University **INVITED**

The advent of cluster ion sources for Secondary Ion Mass Spectrometry (SIMS) has opened new applications for this technique. In particular, the C@super 60+@ ion beam appears to be quite promising as a source for imaging and depth profiling of molecular substrates. From a fundamental point of view, the obvious question is what are the atomic motions that result from the cluster vs. atomic bombardment? Using molecular dynamics computer simulations we have begun to elucidate the basics mechanisms of ejection or sputtering due to C@super 60@ bombardment of solids. Systems investigated to date include a clean Ag substrate,@footnote 1@ a thin film of benzene on Ag@footnote 2@ and

water ice. The various systems investigated to date will be discussed along with relevant experimental data. @FootnoteText@ @footnote 1@ Enhancement of Sputtering Yields due to C@super 60@ vs. Ga Bombardment of Ag{111} as Explored by Molecular Dynamics Simulations, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, Analytical Chemistry, 75, 4402-4407 (2003)@footnote 2@ Microscopic Insights into the Sputtering of Ag{111} Induced by C60 and Ga Bombardment of Ag{111}, Z. Postawa, B. Czerwinski, M. Szewczyk, E. J. Smiley, N. Winograd and B. J. Garrison, J. Phys. Chem. B, 108, 7831-7838 (2004) .

4:40pm **AS-WeA9 Comparison of TOF-SIMS and XPS Analysis Using a C@sub 60@ Ion Sputter Cleaning**, *N. Sanada, T. Miyayama, J.S. Hammond,* ULVAC-PHI, Inc., Japan*; J.F. Moulder, S.R. Bryan,* Physical Electronics
The analysis of chemical layers buried in the near surface region from 1 to 100 nm is of great interest to polymer and biomaterials scientists. However, it has been a great challenge to get chemical information from this region of some materials because of chemical damage observed following ion beam sputtering. Recently, we have applied a buckminsterfullerene (C@sub 60@) ion beam for sputter cleaning and depth profiling to minimize chemical damage for organic and inorganic materials.@footnote 1@ Extremely low sputtering degradation of many organic materials such as polytetrafluoroethylene,@footnote 1@ polyesters, gelatins, and multilayer latex materials@footnote 2@ were observed by XPS. The effects of different C@sub 60@ ion beam accelerating voltages and impact angles on accumulation of residual carbon and chemical damage were examined with XPS using standard samples of polyethyleneterephthalate (PET) and SiO@sub 2@. The quantities of carbon residue in the SiO@sub 2@ film reduced as the increasing accelerating voltages. The impact angle of the ion beam also affected the carbon residue in the film.@footnote 3@ Based on these experiments, an optimized protocol for using a C@sub 60@ ion beam with XPS was developed. We will discuss TOF-SIMS analysis of polymers after sputter cleaning with a C@sub 60@ ion beam under the protocol optimized with XPS. For many polymers, the high energy resolution XPS spectra following C@sub 60@ ion beam exposure showed a constant elemental and functional group stochiometry. The higher sensitivity of TOF-SIMS analysis of these materials allows an examination of more subtle changes induced by the C@sub 60@ ion beam not observed in the XPS analysis. @FootnoteText@ @footnote 1@ N. Sanada et al., Surf. Interface Anal., 36 (2004) 280.@footnote 2@ D. Sakai, et al., J. Surf. Anal. (Tokyo), submitted.@footnote 3@ N. Sanada, et al., AVS 51st. Int. Symp. As-TuM5.

5:00pm **AS-WeA10 TOF-SIMS Imaging of OLED Devices using a Au Cluster Ion Beam**, *S.R. Bryan,* Physical Electronics*; J.S. Hammond, N. Sekiya, A. Yamamoto,* ULVAC-PHI, Inc.
Organic light emitting diode (OLED) technology is a growing research area which may lead to next generation display and lighting commercial products. OLED is based on the use of multi-layers of thin molecular or polymer materials which emit light directly when a voltage is applied. The total thickness of the multi-layer film structure is usually less than 500nm. The organic layers can be doped with specific enhancing molecules to get the desired brightness and color. This new cutting edge technology based on patterned organics requires analytical techniques that can characterize the organic structure of the devices with submicron spatial resolution and good depth resolution. TOF-SIMS offers one of the only techniques that can provide the needed spatial resolution with molecular specificity. One of the most important commercial developments in TOF-SIMS instrumentation in recent years has been the introduction of cluster ion beams for enhancement of organic molecular secondary ion yields. Although Ga+ LMIG sources, which have been used in TOF-SIMS since 1990, has sufficient spatial resolution for most applications, the secondary ion yield of organic molecules from Ga+ sputtering is insufficient for many applications. Development of the Au LMIG emitter, which allows TOF-SIMS analysis with Au+, Au2+ or Au3+, extends the capabilities of TOF-SIMS to image patterned organic materials. The capabilities of imaging with the Au LMIG emitter will be compared to the Ga emitter for characterization of OLED devices. Spatial resolution, damage cross-sections, and ultimate detection limits will be compared between Ga, Au, Au2, and Au3 for typical molecules used in OLED devices.

Applied Surface Science
Room 206 - Session AS+TF-ThM

Thin Film Characterization
Moderator: P.M.A. Sherwood, Oklahoma State University

8:20am AS+TF-ThM1 Characterization of Nanoscale Ceramic Gradient Coatings for Gas Analytical Microdevices, *M. Bruns, V. Trouillet, H. Mueller, E. Nold,* Forschungszentrum Karlsruhe GmbH, Germany*; R.G. White,* Thermo Electron Corporation, England

The key element of the Karlsruhe Micro Nose is a thumbnail sized gas-sensitive microarray which at present consists of 38 sensor elements on an area of 4x8mm@super 2@. It is based on a noble metal-doped SnO@sub 2@ layer, the electrical conductivity of which is highly sensitive to the composition of the ambient atmosphere and is measured between adjacent parallel platinum strip electrodes. In order to enable pattern recognition techniques these initially identical sensors have to be gradually differentiated with respect to their gas response. For this purpose gas-permeable membranes with thickness variation of approximately 2 to 10 nm were deposited across microarray using ion beam assisted deposition. In this work we focus on mixed membranes combining the gas permeability of silica and the chromatographic discriminating capability of alumina. Different geometries were achieved by shaping the ion beam profile to gradually alter the ion current density across the microarray leading to laterally different deposition rates. Various Al/Si ratios within the membranes were obtained using different substrate temperatures during deposition. In the present paper a comprehensive characterization of differently shaped nanoscale membranes is reported. Auger electron spectroscopy is used for evaluation of the geometrical integrity of the uncoated electrode pattern and for the determination of thickness profiles, respectively. Parallel angle resolved X-ray photoelectron spectroscopy provides thickness information for the membranes together with information on chemical binding states in a non-destructive manner. Ellipsometry is presented as a powerful quantification method for the determination of the desired ultra thin membrane thickness profiles. Moreover, after calibration with surface analytical data, ellipsometry allows for rapid evaluation of Al/Si concentrations ratios within the membranes.

8:40am AS+TF-ThM2 Characterization of Low k Dielectrics Using Auger Microprobe Analysis, *C. Dziobkowski,* IBM Corporation, E. Fishkill*; E.D. Adams,* IBM Corporation, Essex Jct.*; J.A. Coffin, R.E. Davis, P.L. Flaitz,* IBM Corporation, Hopewell Jct.*; E.G. Liniger,* IBM Research, Yorktown Heights*; S.E. Molis, D.D. Restaino,* IBM Corporation, Hopewell Jct.

As the dimensions of integrated circuits are reduced, the capacitance between metal lines has an ever increasing impact on device performance. It increases circuit delay, results in parasitic capacitance creating crosstalk, degrades the signal to noise ratio and increases power consumption. Reduction of capacitance by employing low k dielectric materials is thought to be a solution. These low k materials have to be characterized as to their composition, uniformity, void formation and oxygen permeability requirements. This paper gives a description of the methodology developed using Auger depth profile analysis to characterize these new materials. Also important is how these Auger microprobe results can be compared to data obtained from TEM, TOF-SIMS and Rutherford backscattering analyses. The synergism of these analytical techniques is necessary to obtain the understanding needed for the integration of these low k dielectric materials with copper metallurgy in successful device fabrication.

9:00am AS+TF-ThM3 Semiconductor-Dielectric Interfaces: Composition and Structure, *L.C. Feldman, S. Dhar,* Vanderbilt University*; J.R. Williams,* Auburn University*; L. Porter,* Carnegie- Mellon University*; J. Bentley,* Oak Ridge National Laboratory*; K.-C. Chang, Y. Cao,* Carnegie-Mellon University
INVITED

The semiconductor-dielectric interface is the key to a successful MOSFET technology and has played the essential role in the silicon revolution. Wide-band gap materials have presented a challenge to achieve the same degree of interface perfection as silicon, although considerable progress is underway. The SiC/SiO2 interface is of particular scientific interest in this development because of its close relationship to silicon, both in processing and structure. The oxidation process in SiC yields a heavily defected SiC/SiO2 interface giving rise to poor device characteristics. Systematic use of chemical modification and processing, combined with a careful analysis of interfacial structure, results in significant progress in reducing defects and increasing inversion layer carrier density and mobility. For example nitridation of this interface results in a remarkable improvement and is a driving force for understanding the nitrogen profile and concentration. The quantitative nitrogen profile is critical to this understanding and provides a significant depth profiling challenge. Using a variety of probes including medium energy ion scattering, secondary ion mass spectroscopy, nuclear profiling and electron energy loss spectroscopy we show that the nitrogen is confined to within ~1.5 nm of the buried interface, with concentrations that are crystal face dependent and vary from 0.5 to ~1.5 x 10@super 15@/cm@super 2@. From an analysis point of view the significant new finding is the comparison of techniques and the degree of quantitative agreement between the different probes. @FootnoteText@ Supported by DARPA, N00014-02-1-0628 and ONR,N00014-01-1-0616. Research at the O. R. N. L. was sponsored by the Division of Materials Sciences and Engineering, U.S. Department of Energy, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

9:40am AS+TF-ThM5 Comparison of Silicon Oxynitride Produced by PIII/D and Reactive Sputtering, *N.D. Theodore,* M. Bagge-Hansen, B.C. Holloway, *D.M. Manos,* College of William and Mary*; C. Hernandez, T. Siggins, H.F. Dylla,* Jefferson Lab

High-purity, hydrogen-free silicon oxynitride films were successfully created using two techniques, plasma immersion ion implantation/deposition (PIII/D) and reactive sputtering. Our previous work has shown that coating 6" polished 304 stainless steel electrodes with silicon oxynitride, created by PIII/D, dramatically reduces field emission from 27 μA of at 15 MV/m to 160 pA at 30 MV/m. We have recently developed a new procedure to deposit silicon oxynitride without ion implantation using a low temperature (<200°C) Rf reactive sputtering process. Both procedures use a 750 W inductively-coupled nitrogen plasma that sputters silicon dioxide from a quartz dielectric window. The purpose of this study was to determine and compare the composition and electrical properties of the silicon oxynitride coatings created using the reactive sputtering and PIII/D procedures. The homogeneity, stoichiometry, and density of deposited/implanted layers were determined using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR), and Rutherford backscattering spectrometry (RBS). AES depth profiles determined that both procedures created homogeneous films, and FTIR and XPS spectra confirmed the creation of silicon oxynitrides with approximately 10% nitrogen. Ultraviolet photoelectron spectra and capacitance-voltage measurements will also be presented and discussed.

10:00am AS+TF-ThM6 Microbridge Testing of Plasma Enhanced Chemical Vapor Deposited Silicon Oxide Films on Silicon Wafers, *Z. Cao,* Boston University*; T.-Y. Zhang,* Hong Kong University of Science and Technology*; X. Zhang,* Boston University

Plasma-enhanced chemical vapor deposited (PECVD) silane-based oxides (SiOx) have been widely used in both microelectronics and MEMS (MicroElectroMechanical Systems) to form electrical and/or mechanical components. During fabrication of such microelectronic and MEMS devices, PECVD SiOx undergo many thermal cycles, which often causes unwanted changes in thermal-mechanical properties of the material, and consequent degradation of device performance and reliability. In this paper, a novel nanoindentation-based microbridge testing method for thin films is proposed to measure both the residual stresses and Young's modulus of PECVD SiOx thin films. In this method, freestanding microbridges are fabricated from the thin films using the micromachining techniques. The tests are performed at the center of the microbridges with an instrumented nanoindentation system and the load-deflection curves are recorded. Our theoretical model used a closed formula of deflection vs. load, considering both substrate deformation and residual stress in the thin film. To simulate real thermal processing in device fabrication, some microbridges underwent various rapid thermal annealing (RTA) at temperatures up to 800ºC. An interferometric microscope was also used to measure the curvature profiles of the bridges. Together with nanoindentation test results on the microbridges, we were able to decide the changes in residual stresses and Youngâ?Ts modulus of the PECVD SiOx thin films under different thermal annealing. Two factors, density change and plastic deformation, were identified as controlling mechanisms of stress changes in the films. A microstructure based mechanism elucidates "seams" as source of density change and "voids" as source of plastic deformation, accompanied by viscous flow. This mechanism was applied to explain our experimental results of thermal annealing of PECVD SiOx films.

10:20am AS+TF-ThM7 Characterization of Ultra Shallow Arsenic Implants by ARXPS, LEXES, MEIS, and Dynamic SIMS, *G. Conti, Y. Uritsky, H. Graoui, M. Foad,* Applied Materials*; C.R. Brundle,* Brundle & Associates*; D. Kouzminov,* Materials Analytical Services*; C. Hitzman,* Full Wafer Analysis*; P. Mack, J. Wolstenholme,* Thermo Electron Inc., UK

Ultra-shallow As implants are a leading-edge technology. Low voltage results in implant layers of tens of A thickness after anneal. Reliable metrology for shallow implants is needed. We characterize the implant layer as a function of nominal dose (1E14 to 2E15 ions/cm2) at 2KV, using a variety of techniques. Angle Resolved-XPS gives precise measurement of SiO2 oxide thickness, monitors the chemical state of As, and gives a non-destructive rough depth profile. Low Energy X-Ray Emission Spectroscopy, LEXES, gives a non-destructive As dose measurement, which depends on calibration against a bulk standard, for accuracy. MEIS gives a non-destructive depth distribution of atoms not in Si substitutional sites, and a dose calibrated by reference to amorphised Si. Dynamic SIMS provides very precise dose and depth distribution measurement to very low As concentrations, but is destructive and has a problem with the initial part of the depth scale and any As dose within it. Taken together a complete picture of the implant layer is obtained. Prior to annealing the As has a broad distribution, centered at about 50A depth. The outer oxide layer increases from 13A at 1E14 ions/cm2 dose to 18A for 2E15 ions/cm2 dose. ARXPS showed that samples from one particular implanter had a component of As2O3 very near the surface, well removed from the elemental As implant. The annealing conditions (N2 with 10% O2) double the oxide thickness (22A at 1E14 ions/cm2 dose; 38A at 2E15 ions/cm2), and cause the As to pile up just on the Si side of the SiO2/Si interface, but with a strong diffusion tail to 150A depth (SIMS). XPS shows that any oxide component is eliminated by anneal. A comparison of the MEIS to the SIMS depth distributions shows that the diffusion tail is in substitutional sites, and therefore not observable in the MEIS.

10:40am AS+TF-ThM8 Hot Electron Transport Across Manganese Silicide Layers on the Si(001) Surface, *A. Stollenwerk, M.R. Krause, V.P. LaBella,* University at Albany SUNY

The need for high efficiency spin injection for spintronic applications has led to the study of different ferromagnetic interfaces. Recent theoretical studies have shown that the MnSi interface orders ferromagnetically.@footnote 1@ We performed ballistic electron emission microscopy (BEEM) on the MnSi/Si(001) Schottky barrier to study the hot electron transport properties. BEEM allows the interface to be probed on the nanometer scale and also gives the option to perform spin dependent measurements. Samples for this study were fabricated by electron beam deposition of Mn onto n-type Si(001) with thicknesses ranging from 50 to 200 Å. These layers were annealed at various temperatures in ultra high vacuum (UHV). The front side contact was fixed ex situ before the sample was reinserted into UHV to perform BEEM. Film composition has been determined by secondary ion mass spectroscopy (SIMS). The Schottky heights have been determined by fitting the BEEM spectra to the Bell-Kaiser model. The effects of temperature, film thickness and composition on the BEEM current will be discussed. @FootnoteText@ @footnote 1@S.A. Wolf et al., Science 294, 1488 (2001).

11:00am AS+TF-ThM9 Optimization and Deposition of CdS Thin Films As Applicable to TiO@sub2@/CdS Composite Catalysis, *K. Prabakar, T. Takahashi,* Toyama University, Japan*; T. Nakashima,* Kashiwa Chuo High School, Japan*; Y. Kubota,* Yokohama City University, Japan*; A. Fujishima,* Kanagawa Academy of Science and Technology, Japan

Recently, the study of interparticle electron transfer between dissimilar semiconductors has received interesting investigations. Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large bandgap and energetically low-lying conduction band by another one having a small band gap and energetically high-lying conduction band. In our investigations, photosensitization of TiO@sub2@ by narrow band gap semiconductor such as CdS have been investigated and found to be effective for separation and transfer of photoexcited charge carriers. The TiO@sub2@ thin films were deposited by direct current reactive magnetron sputtering and CdS by chemical bath deposition. Thin films of CdS were deposited from a solution of analytical grade CdSO@sub4@ (1 M) and thiourea (1 M) in an alkaline solution of ammonia with a total volume of 80 ml. The temperature and time of the deposition were varied between 65 to 80 ° C and 30 to 60 minutes respectively. To vary the composition of the films, different concentrations of CdSO@sub4@ and thiourea were used. The optical band gap energy varied from 2.41 to 2.59 eV as the CdSO@sub4@ solution concentration increased from 0.4 to 2.8 ml while keeping the thiorea as 1.6 ml. The as deposited films were annealed at different temperatures to study the effect of structural (XRD) and surface properties (SEM and AFM) on the efficiency of the TiO@sub2@/CdS catalysis. The TiO@sub2@ films were found to be polycrystalline anatase structure with optical band gap energy of 3.1 eV. The degradation efficiency under visible light of methanol and methylene blue by TiO@sub2@/CdS films were investigated by FTIR and spectrophotometer respectively and the results are discussed in details. The visible light photocatalytic degradation efficiency TiO@sub2@/CdS is far higher than that of TiO@sub2@ film.

Applied Surface Science
Room 206 - Session AS+TF-ThA

Thin Film Characterization II
Moderator: K. Lloyd, Dupont

2:00pm AS+TF-ThA1 C@sub n@ (50@<=@n<60) Films on HOPG, *A. Böttcher, P. Weis, S.-S. Jester, D. Löffler, M.M. Kappes,* Universität Karlsruhe, Germany

Novel solid materials have been grown under ultra high vacuum conditions by gentle deposition of C@sub n@@super +@ (50@<=@n<60) on HOPG surfaces (kinetic energy typically < 0.1 eV/atom). C@sub n@@super +@ ions resulting from the electron-impact induced ionization/dissociation of C@sub 60@ are driven by a system of electrostatic lenses through a mass spectrometer towards the HOPG substrate where an appropriate retarding potential assures their soft-landing. This setup enables to achieve deposition rates in the range of 10@super 12@ ion/s. AFM images reveal that the C@sub n@ films grow according to the Volmer-Weber scenario, i.e. the surface is initially dominated by 2D fractal islands, which in later deposition stages become 3D dendritic pyramids. This behavior stems from the aggregation of C@sub n@ cages, which is driven by reactive sites as formed by adjacent pentagons (or heptagons) on individual cages. The resulting covalent bonds are responsible for the unusually high thermal stability of the C@sub n@ films. Thermal desorption spectra of C@sub 58@ reveal activation energies around 2.2 eV, which are considerably higher than the sublimation enthalpy of C@sub 60@ films. AFM images taken after completing the desorption exhibit a network of highly polymerized cages, which remains stable even at temperatures around 1300 K. Recent DFT calculations as well as UPS-measurements support the aggregation scenario of C@sub n@ cages. Well recognizable features in the valence-band spectra allow identification of the band gap as well as contributions from C@sub n@-C@sub n@ bonds.

2:20pm AS+TF-ThA2 An in situ Study on Amorphous Carbon Films and the Vapor Phase Lubrication in Magnetic Data Storage Media, *Y. Yun, A.J. Gellman,* Carnegie Mellon University

Amorphous carbon films have been used as a protection for the magnetic layer in hard disks for years. Perfluoropolyalkylether (PFPE) has been applied on the amorphous carbon film surface as lubricant during the crashing of the read-write head on the amorphous carbon film. The fundamental understanding of the thermal stability and oxidation kinetics of amorphous carbon films and the adsorption of PFPE lubricants is essential to obtain the ultimate high performance protection and lubrication. Vapor phase lubrication integrates the amorphous carbon film deposition and lubrication in vacuum. The amorphous carbon film can be oxidized under controlled conditions immediately prior to lubricant adsorption. The kinetics of oxidation has been studied using x-ray photoelectron spectroscopy in an UHV apparatus that allows oxidation of freshly deposited amorphous carbon films. The dissociative sticking coefficient of oxygen is ~10-6 and the oxidation kinetics can be described by a Langmuir-Hinshelwood mechanism. The vapor phase lubrication of amorphous carbon film has been emulated by absorbing (CF3CF2)2O and CF3CH2OH that serve as models for the fluorinated ether backbone and hydroxyl endgroup of PFPE lubricants. No decomposition was observed. The desorption energy of the hydroxyl endgroup is sensitive to the oxidation of the amorphous carbon film by air or O2. The increase of the desorption energy is proportional to the oxygen content on the amorphous carbon film surface. This indicates that the interaction between PFPE lubricant and the amorphous carbon film can be tailored by controlled oxidation of the amorphous carbon film. Vapor phase lubrication not only helps to probe the bonding mechanism of PFPE lubricant with amorphous carbon film, but also proposes a lubrication method which allows people to design and tune the bonding of PFPE lubricants with amorphous carbon films by controlled oxidization.

2:40pm AS+TF-ThA3 Laser Processing of Polymer Nanocomposite Thin Films, *A.T. Sellinger, E.M. Leveugle, G. Peman, L.V. Zhigilei, J.M. Fitz-Gerald,* University of Virginia

Current biotechnology and sensor research has enhanced the drive to establish viable methods for depositing high quality organic and polymer thin films. In this research, solid targets of polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly-lactic co-glycolic acid (PLGA) were prepared for room temperature pulsed laser deposition (PLD). Likewise, frozen targets consisting of varying concentrations of PS, PMMA, and PLGA dissolved in a volatile matrix material were prepared for matrix assisted pulsed laser evaporation (MAPLE). Carbon nanotubes (CNTs) were subsequently added to both PLD and MAPLE target systems in upwards of 20 wt.% loading for deposition of polymer nanocomposite films. Targets were ablated using a 248 nm KrF laser at fluences ranging from 0.025 J/cm@super 2@ to 1.0 J/cm@super2@. In addition, polymer concentration in MAPLE targets was varied between 1 wt.% and 10 wt.% relative to the matrix solvent. Films were deposited on Si, SiO@sub 2@, and NaCl substrates at room temperature in an Ar atmosphere. The chemical properties of the films deposited by both methods varied significantly from the native, with changes in molecular weight on the order of 75%. While PLD produced films generally showed little observable morphology, MAPLE deposited films typically showed evidence of blistering. A molecular dynamics (MD) program developed to simulate ablation of a frozen target during MAPLE was utilized to model and predict experimental phenomena. Particularly, the ejection of clusters of PMMA and volatile matrix molecules was studied and related to the observed morphology of the deposited films.

3:00pm AS+TF-ThA4 Thin Films of Fe on Pt(111) : Alloy Formation, *M. Yoshimura, S. Komaru, K. Ueda,* Toyota Technological Institute, Japan

Addition of transitional metals to Pt catalysts has been known to improve catalytic efficiency. Pt-Fe bimetallic catalysts attract attention in industrially important fields such as polymer electrolyte fuel cell (PEFC).@footnote 1@ Modification of geometrical and electronic structure of Pt surface would be responsible for the improved efficiency. Recently, Jerdev et al. examined Fe-Pt alloying processes by XPS and LEED.@footnote 2@ They found that heating thick Fe films on Pt result in an ordered alloy layer of 2 x 2 structure. However, detailed atomistic study has not been carried out. Here, we report scanning tunneling microscopy (STM) study on the growth of Fe on Pt(111) and the alloying processes by heating. All experiments were performed in ultrahigh vacuum of a base pressure below 2 x 10@super -8@ Pa. Pt surface was cleaned by cycles of Ar@super +@ ion bombardment at 1 keV and subsequent annealing in vacuum to 1300 K. Surface cleanliness was monitored by XPS and STM observation. Fe (99.999 %) was deposited onto the Pt(111) surface by an e-beam evaporator. STM observation was carried out at room temperature, and electrochemically etched tungsten tips were used. After 1.1 ML Fe deposition at room temperature, two-dimensional Fe islands up to three stories were formed and the Pt substrate was still visible, which is reasonable in terms of surface free energy. After annealing to 800 K, diffusion of Fe occurs and a network structure consisting of Fe and Pt atoms appears on the surface. After annealing to 1070 K, 2 x 2 structure was locally formed at the step edges, which corresponds to the reported alloy structure by Jerdev et al. It is also found that the surface includes defective structure as well as phase boundaries. The growth of Fe on Pt(111) as well as detailed alloying processes are discussed. @FootnoteText@ @footnote 1@ L-J. Wan et al., Chem. Comm. 2002 (2002) 58.@footnote 2@ D. I. Jerdev et al., Surf. Sci. 513 (2002) L391.

3:40pm AS+TF-ThA6 Scanning Auger Microscopy of Alkylated Crystalline Silicon(111) Surfaces, *H.M. Meyer III,* Oak Ridge National Laboratory; *L.J. Webb,* California Institute of Technology; *D.F. Paul,* Physical Electronics; *N.S. Lewis,* California Institute of Technology

Silicon materials used in solar energy conversion devices must be prepared to a high degree of purity in order to prevent recombination of the photoexcited electron-hole pair. Recently, a wet chemical alkylation technique has been shown to result in an atomically-flat surface covered with bound alkyl groups preventing complete formation of silicon oxides at the surface even after exposure to oxidizing environments over long time periods. Surface charge carrier recombination velocities remain remarkably low, indicating that silicon oxides forming do not result in charge carrier trap states as previously observed on un-passivated, hydrogen-terminated Si(111). These results indicate that any detectible oxide is not growing in a uniform manner, but rather in small patches leaving large portions of the alkylated surface free of any oxide. Extensive x-ray photoelectron spectroscopic evidence on the chemical structure and reactions of these passivated surfaces has been collected over large areas of the surface. Scanning Auger microanalysis was used to map the oxidation of alkylated Si surfaces to determine if it was proceeding uniformly or in discrete areas. Preliminary results using a PHI 680 Scanning Auger Nanoprobe showed distinct patches of oxide less than 100 nm in width. The orientation of the oxide patches suggested that growth was occurring along step edges between flat terraces, leaving the terraces themselves chemically unaltered. Comparison of these early results were made with data obtained using PHI 700 Field Emission Scanning Auger Nanoprobe, a higher performance Auger Electron Spectroscopy (AES) system. The PHI 700 Schottky field emission optics offer Auger spatial resolution of less than

8nm and made it possible to image the oxide features more clearly. Further, the PHI 700 was able to image areas with comparable resolution as the PHI 680, but with less current and therefore less alteration of the oxide due to electron beam reduction.

4:00pm AS+TF-ThA7 Electron Beam Induced Processes for Repairing Defects on Quartz Masks, *M. Fischer, J. Gottsbachner, S. Mueller, E. Bertagnolli, H.D. Wanzenboeck,* Vienna University of Technology, Austria

For conventional optical masks focused ion beam (FIB) has become a popular tool for repairing defects. A fundamental problem of using FIB for mask repair is the implantation of Ga-ions and the damage of the substrate surface. Especially for 248 nm and 193 nm lithography electron beam repair avoids the transmission loss which is generated by the implanted Ga-ions. This paper presents some promising results that demonstrate the feasibility of using electron beam induced processes for repairing defects on quartz masks. A commercial scanning electron microscope with a tuneable acceleration voltage of 0,1- 30 kV equipped with a gas inlet system was used to investigate a siloxane based deposition process of silicon oxides on quartz glass substrates. Siloxane together with an oxidizing reagent is decomposed by the electron beam on the surface of the quartz glass substrate. The process was optimized towards high material purity. A chemical investigation of the deposited structures was performed by Auger electron spectroscopy and EDX. The optical properties of the deposited material were investigated by infrared, UV/Vis and AIMS measurements. The influences of process parameters such as precursor gas combinations, precursor gas composition ratios, and electron beam parameters on the optical transparency were discussed. The electrical features of the deposited silicon oxide as dielectric material were tested with a metal-insulator-metal setup. A correlation between the electrical properties, the material purity and the optical transparency of the deposited silicon oxide structures is discussed. This work is considered a solid bias for a better understanding of electron induced deposition of silicon oxide and path the way of a further process optimization of this quartz glass mask repair technique.

4:20pm AS+TF-ThA8 Extending Defect Root-Cause Analysis to sub-100nm in-film Particle Contamination, *C. Lazik, Y. Uritsky,* Applied Materials, Inc.

Scanning Electron Microscopy (SEM) in combination with Energy Dispersive X-Ray Spectroscopy (EDX) is essential for effective root-cause particle analysis in the semiconductor industry and forms the core of commercial defect review tools (DRT). In many cases, however, particularly for small (<0.1μm) in-film particles located within or under deposited films, the standard DRT approach is less straightforward because of (i) uncertainty in the position of the defect 'core' within the film and/or (ii) poor SEM contrast in dielectric films. These effects ultimately limit the assurance that the electron beam is focused on the defect "core" during automated spectrum acquisition. In addition, the defect geometry may preclude the subtraction of an EDX background spectrum. We present here several examples related to the analysis of ~ 50nm "bump" defects, each of similar surface morphology, encountered following the deposition of one or more dielectric films. Providing a suitable analysis of the particle cross-section enabled the classification of the defect based upon its location within the film-stack as well as the defect formation mechanism (e.g. gas-phase nucleation, arcing). In each case, the defects were analyzed initially by top-down SEM/EDX followed by cross-sectional analysis using the focused ion beam (FIB) with only limited success. Extended Auger (PHI Smart-300 DRT) and/or TEM analysis on FIB prepared samples proved critical in yielding accurate root-cause analysis. Details will be discussed in presentation, but the general conclusion is that the integration of FIB/TEM into the modern DRT platform is necessary.

Applied Surface Science
Room 206 - Session AS-FrM

Practical Methods and Applications for Surface Analysis
Moderator: M.C. Burrell, GE Global Research Center

8:20am AS-FrM1 ToF-SIMS Measurements of a Fluorocarbon-based Self-Assembled Monolayer on Si, *J.A. Ohlhausen, K.R. Zavadil,* Sandia National Laboratories
Low surface energy coatings and films are needed to minimize stiction, high friction and wear of the oxide-terminated silicon-based MicroElectroMechanical Systems (MEMS) to ensure reliable device function. One common approach is to deposit self-assembled monolayer (SAM) films containing reactive silane headgroups and low energy pendant chains to cover the complex structures used in MEMS devices. The composition of these films is difficult to characterize and quantify (a property or quality is quantified composition, an aspect of structure, etc.). Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an ideal tool for characterizing these types of films, however interpretation of the spectral data generated is complex and challenging. We are using the combination of X-ray Photoelectron Spectrometry (XPS) and ToF-SIMS to detect and quantify several candidate fluorocarbon-based SAMS on Si coupons and on MEMS devices. Unexpected fragmentation caused by the interaction of the primary ion beam with the fluorocarbon chain in contact with the Si surface creates ions whose presence are not intuitive. We can account for these ion fragments and use them to aid in quantifying the film composition. Our methods include the use of coverage-dependent fragmentation signatures along with the application of multivariate statistical techniques to establish the co-variance in these signatures. The fragmentation seen in this system along with the quantification method we used will be presented. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energys National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:40am AS-FrM2 XPS-imaging; Investigation of the Potentials of a Recent Algorithm Applied to a Patterned Polymer, *S. Hajati,* University of Southern Denmark*; S. Tougaard,* University of Southern Denmark, Denmark*; S.J. Coultas, C.J. Blomfield, C. Moffitt,* Kratos Analytical Ltd, UK
We have investigated the practical potentials of a recent algorithm for automatic data processing of XPS spectra.@footnote 1@ For each XPS peak, this algorithm determines the total amount of the corresponding atoms within the outermost ~ 3 inelastic electron mean free paths and it also gives an estimate of their depth distribution. The validity of the algorithm was recently tested@footnote 2@ by analysis of conventional (low lateral resolution) XPS measurements from layered samples. It was found to be very accurate and robust and much superior to usual analysis which relies on peak areas. In this paper we have studied spectra acquired at high lateral resolution (~2μm) of a patterned hydrophilic plasma polymer deposited on to a PTFE substrate. The spectra are reconstructed from a series of parallel photoelectron images recorded using a pulse counting delay line detector. For each pixel, we have used the C1s, F1s and O1s peaks to determine the amount of atoms as well as their approximate depth distribution for each element. The method is less accurate than the traditional QUASES-peak shape analysis method. However the latter requires operator interaction and is not practical for XPS imaging where thousands of spectra must be analyzed. @FootnoteText@ @footnote 1@ S. Tougaard, J. Vac Sci. Technol. A21, 1081 (2003)@footnote 2@ S. Tougaard, J. Vac. Sci. Technol. 2005, In press .

9:00am AS-FrM3 Surface Analysis in Modern Industry - More, Faster, Cheaper, Better?, *I.W. Fletcher, S.F. Davies,* ICI plc, UK   **INVITED**
The driving aim of most industrial activity is to make money by producing and selling products that people need or want and many processes and products involve surfaces or surface chemistry issues where surface analysis can deliver significant benefits. Research and development along with process and product problem solving are the obvious areas, although SHE, patent protection and various legal applications are also important. There is pressure on most businesses to increase profitability and to reduce costs, with analysis all too often being seen as pure cost. The 'do more, faster, cheaper' requirement may seem to conflict with the unwritten requirement to 'do it right'. Industrial analytical problems can and do provide significant challenges, often pushing analysts, instrumentation and techniques to the limits of what is possible. Fortunately modern equipment is now more reliable, often automated and is also capable of producing better quality data with much higher signal to noise levels and with better

resolution than before. These help with the speed and accuracy of analysis and also open up new areas of information that were previously inaccessible. For example, images of the various species on the surface can be critical to a complete understanding of the situation and to many product developments. Using static SIMS with polyatomic and cluster ion beams, it is now routinely possible to generate images from truly molecular species rather than from elemental or small fragment ion species. This presentation will outline several practical examples using SSIMS and XPS applied to 'industrial' samples including man-made fibres, hair, foodstuffs and catalysts.

9:40am AS-FrM5 Comparison of Methods for the Quantification and 3D Characterization of Polymer Blends using XPS and CLSM, *J.L. Fenton, K. Artyushkova, J.E. Fulghum,* University of New Mexico
The complete characterization of a heterogeneous polymer blend often requires multiple analytical techniques; each of the techniques providing limited data compared to the total information required. The most effective approach to multitechnique analysis utilizes data acquired from the same area on the same sample. However, there are still a number of issues to be resolved if quantitative multitechnique fusion is to be utilized. This study evaluates methods for quantifying phases observed in confocal laser scanning microscopy (CLSM) images. CLSM images can have a lateral resolution comparable to or better than XPS images, provide information on fluorescent polymer phase distribution, and 3D volumes can be created by changing the focal plane. In this talk we evaluate the use of CLSM images to quantitatively investigate phase distributions in polymer blends as a function of depth. CLSM image quantification methods including using image intensity calibration beads with vertical polymer blend distribution standards, analytical treatment of CLSM optics and fluorescence properties, and correlation with XPS images are compared. The quantitative concentration data is then used to create a 3D volume containing chemical and elemental concentration information. This work has been partially supported by NSF CHE-0350666, the UNM NSF IGERT CORE DGE-00114319 and UNM.

10:00am AS-FrM6 X-ray Photoelectron Spectroscopic Study of an Oxygen-doped Zinc Sulfide Surface Using Sample Biasing, *Y.-Q. Wang, P.M.A. Sherwood,* Oklahoma State University
X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of zinc sulfide (ZnS) exposed to a number of oxidation treatments at various conditions to understand the effect of oxygen on surfaces of II-VI compounds. These compounds are widely used as luminescence and window materials, where the mechanism of the effect of oxygen interaction and its effect on the properties and applications of these materials, has not been clearly understood. The oxygen was introduced onto the ZnS surface by heat-treating the sample in a furnace with water vapor and by synthesis of ZnS. The core XPS studies were conducted with and without the application of a sample bias potential, and showed that oxygen interaction caused a considerable change in the surface chemistry of ZnS. The application of a positive bias led to a shift in the core XPS peaks expected for a conductive material, but the negative bias gave rise to unusual behavior. In the case of ZnO the core XPS peaks behaved in the way expected of a conducting material under positive or negative bias. The ZnS samples exhibited a peak shift that was closely related to the oxygen content in the surface region. Furthermore, the sample synthesized in aqueous solution resulted in peak splitting under a negative bias. The surface chemistry monitored by XPS, and the interpretation of the biasing shifts allows for a better understanding of the change of luminescence phenomena in ZnS materials involving oxygen.

10:20am AS-FrM7 Thin Oxide Free Phosphate Films of Novel Composition formed on the Surface of Vanadium Metal and Characterized by X-Ray Photoelectron Spectroscopy, *D.J. Asunskis, P.M.A. Sherwood,* Oklahoma State University
This paper reports the preparation of thin (less than 100 Angstroms) oxide-free phosphate films of various compositions on vanadium metal. These films are interesting because of their potential for corrosion inhibition, adhesion promotion and biocompatibility. Valence band and core-level X-ray photoelectron spectroscopy (XPS) were used to characterize the films. The valence band spectra obtained were compared with spectra generated from band structure calculations for various vanadium phosphates and from previously reported spectra of vanadium phosphates. Novel vanadium phosphate coatings were created by the reaction of vanadium metal and different phosphorus-oxygen containing acids, H_3PO_4, H_3PO_3, H_3PO_2 and $H_4P_2O_7$. The paper focuses upon the valence

band region which shows significant differences between the three vanadium phosphate films formed as well as clear differences between the three phosphates and vanadium oxides. The valence band spectra are effectively interpreted by band structure calculations. @FootnoteText@ The work was supported by the National Science Foundation under Grant No. CHE-0137502.

10:40am AS-FrM8 Surface Characterization of Metal Exchanged Mesoporous Materials, *S.G. MacKay,* University of Maine, US*; K.D. Bishop, B.K. Schaefer, J.D. Anderson, J.C. Bolton, H.H. Patterson,* University of Maine

We are investigating the role of transition metal clusters in heterogeneous photocatalysts used for the remediation of a variety of toxic organic compounds. These catalysts have already been successfully employed in remediating organophosphorous and carbamate compounds,@footnote 1@ and they have also been shown to be robust in the presence of dissolved organic carbon.@footnote 2@ The design of these catalysts involves incorporating metal ions into mesoporous materials via ion exchange. Manipulation of the support material geometry and the metal ion composition provides control over the catalyst selectivity and reactivity. Currently we are expanding our application areas to include biological target molecules and organisms. For these studies we have covalently attached zeolite and MCM photocatalysts onto a polymer surface using a methacryl silane. XPS was used to study both the catalyst/polymer attachment chemistry as well as the surface oxidation states of the photocatalytic metal sites. Catalysts studied include faujasite zeolites at different Si/Al ratios exchanged with Ag as well as with mixed metals (Ag/Cu). The correlation of these results with earlier published work using photoluminescence will be shown along with data from both TOF-SIMS and high resolution TEM analyses of these same materials. @FootnoteText@ @footnote 1@J. Phys. Chem. B. 2001, 105, 7508-7516.@footnote 2@Envir. Sci. Technol. 2003, 37, 2280.

11:20am AS-FrM10 Improving High Resolution AFM Images - When are Sharp Tips Worthwhile?, *C.F.H. Gondran,* ATDF Inc., a subsidiary of SEMATECH*; D.K. Michelson,* ISMI, a subsidiary of SEMATECH

Recently, AFM probes with sharper tips (1-2 nm radii of curvature) have become commercially available. This provides broad access to an opportunity to improve high-resolution images. Under the right circumstances, these improvements are very dramatic.@footnote 1@ However, in other instances, sharp tips offer limited benefits and the additional cost may not be justified. This study is designed to improve our understanding of the benefits of using sharp tips and to help determine when these benefits can be realized. Two-dimensional geometric models@footnote 2@ are used to evaluate the effect of tip shape on AFM images, roughness values, and power spectral density curves obtained for a variety of sample types. The effects of tip size are studied as a function of the sample's surface roughness, average feature size, average feature spacing, and surface feature shape. The results, particularly for roughness values, are not always intuitive. The simulated data are correlated to sample data obtained on films commonly used in research and development for semiconductor manufacturing: epitaxial Si, high-k, low-k, and barrier layer materials. These correlations are used to assess the value of sharp tips for the semiconductor industry. @FootnoteText@ @footnote 1@ D. Klinov, S. Magonov "True molecular Resolution in Tapping-Mode Atomic Force Microscopy with High-Resolution Probes," Applied Phys. Letts., 84(14) 2004, p. 2697.@footnote 2@ C. F. H. Gondran, D. K. Michelson "Sampling and Reference Considerations for Very High Resolution AFM Analysis," in Proc. 30th International Symposium for Testing and Failure Analysis, ASM International, Ohio, 2004 p. 357.

11:40am AS-FrM11 Microscopy Study of Composites Based on Propylene-Ethylene Copolymers, *L.L. Ionescu-Vasii,* P. Wood-Adams, Concordia University, Canada*; E. Duschene,* Ecole Polytechnique de Montréal, Canada

MMany recent developments in polymer materials science have been triggered by the development of improved synthesis methods. As a consequence, a wide variety of polymers with unusual properties can be designed and synthesized. Recently, The Dow Chemical Company developed a new catalyst which allows copolymerization of propylene with various alpha-olefin comonomers over a broad range of compositions in isotactic fashion and with high molecular weight (SWOGGER K et al, 2003). Our interest focuses on a new family of propylene-ethylene copolymers produced by Dow Company, which has an exceptional ability to accept very high loadings (80% wt and higher) of fillers or/and additives, while maintaining good processability. The new propylene-ethylene (P/E) copolymers used in our study exhibit high molecular weights, low densities,

relatively narrow molecular weight distributions and unique micro-molecular structures. The ethylene content of these copolymers ranges from 9 to 15 wt %. We report here the first results of our microscopy study of twelve composites (with 20, 40, 60 and 80 wt% calcium carbonate filler) based on three new propylene-ethylene copolymers. Different microscopy techniques (SEM, TEM, AFM) and different samples' preparation techniques (cryogenic microtomy, FIB, annealing) were used in order to obtain a thorough understanding of the microstructure of the composites studied and to evaluate the interaction between the filler particles and the polymer matrices. @FootnoteText@ @footnote 1@ SWOGGER K. W., POON B., ANSEMS P., CHUM S., HILTNER A. AND BAER E. (2003), Material classification and applications of new propylene-ethylene copolymers. SPE ANTEC Tec. Papers, 1768.

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