

Monday Morning, November 3, 2003

Applied Surface Science

Room 324/325 - Session AS-MoM

Practical Surface Science

Moderator: P.M.A. Sherwood, Kansas State University

8:20am **AS-MoM1 Aqueous-derived Planar Proxies: A Connection between Surface Science and Real World Catalysts**, *C.F. Conrad*, Virginia Institute of Marine Science; *C.J. Chisholm-Brause*, *M.J. Kelley*, College of William & Mary

Real catalysts typically comprise metal or metal oxide nanoclusters on a high-surface area insulator oxide support, prepared by aqueous chemistry. Researchers seeking to overcome the experimental difficulty of studying such materials with surface science techniques have made model catalysts by physical deposition, akin to microfabrication technology. It has now become possible to prepare planar proxies by all-aqueous methods, closely akin to those for real catalysts. After obtaining a hydrous gamma alumina layer on a metal foil, established aqueous solution techniques were used to prepare planar proxy and high surface area materials together. To verify their equivalence, both sets of materials were examined by ToF/SIMS, XPS, SEM/EDS and EXAFS, and by response to organic probe molecules.

8:40am **AS-MoM2 The Role of XPS in Materials Characterization in an Industrial R&D Setting**, *M.C. Burrell*, GE Global Research **INVITED**

X-ray photoelectron spectroscopy (XPS) is a widely used method in fundamental surface science and applied materials characterization. As an analytical technique, XPS is an integral part of a modern materials research laboratory. Characterization of complex materials usually requires combinations of analytical methods to provide an understanding of structure-property relationships. In this talk, I will review the types of information provided uniquely by XPS, and illustrate how this information is coupled with data provided from other methods in the characterization of surfaces and thin films. Some examples will be selected from the author's own experience as an XPS expert within a larger materials characterization group at a major industrial R&D site. In this setting, a wide variety of sample types and issues are encountered. The variable degrees of success in the application of XPS to quantitative analysis, determination of oxidation states and functional groups, and thin film compositions will be described. In addition, the current and prospective applications in emerging fields such as biotechnology and nanotechnology will be discussed.

9:20am **AS-MoM4 Quantitative Depth Distribution Analysis of Hg and Na in Glass**, *T.A. Dang*, *T.A. Frisk*, *M.W. Grossman*, *C.H. Peters*, Osram Sylvania
Fluorescent lamps use mercury for efficient conversion of electrical power to light. During lamp operation, some Hg is consumed through interaction and/or deposition on lamp components. One of the primary sites for interaction is the soda lime glass used as a lamp tube. The association of Hg and Na from the glass has been observed by XPS mapping.^{@footnote 1@} It is of particular interest to also evaluate the relationship of these two elements in deeper layers. A depth distribution analysis of Hg and Na would readily provide such information. It has always been a challenge to obtain the depth distribution of Na in glass using sputtering techniques. Due to the high mobility of Na, a soft sputtering condition, which minimizes Na diffusion, is generally required. Unfortunately, this also decreases the sensitivity for Hg, whose intensity is several orders of magnitude lower than that of Na. Simultaneous measurement of Na and Hg is strongly desirable because of the non-uniform nature of the interaction. In this presentation, we are going to compare the depth distribution analysis of Na and Hg using Secondary Ion Mass Spectrometry (SIMS) and High-Frequency Square-Wave Sputtered Neutral Mass Spectrometry (HFSW-SNMS). The advantages and disadvantages of each technique will be discussed. Samples included in the evaluation are composed of both quartz and soda lime glass wafers implanted with Na and Hg respectively as well as the real soda lime glass lamp tube subjected to normal lamp operation.
^{@FootnoteText@ @footnote 1@} T. A. Dang, T. A. Frisk and M. G. Grossman, *Anal. Bioanal. Chem.*, 373, 560 (2002).

9:40am **AS-MoM5 Rutherford Backscattering Quantification of Mercury Interaction with Fluorescent Lamp Materials**, *C.H. Peters*, *M.W. Grossman*, *T.A. Dang*, *T.A. Frisk*, Osram Sylvania Inc.

Understanding mercury interactions with lamp materials is essential to reducing the amount of Hg required for operation of fluorescent lamps as well as improving light output. Rutherford backscattering spectrometry (RBS) is especially well suited to quantification of heavy elements such as Hg or Ba in a light matrix (e.g. soda lime glass). It provides quantitative

measurement of trace amounts of mercury and non-destructive depth distribution information. We have developed a method to quantify buried Hg layers in glass under intact 1 to 2 μm thick alumina particulate coatings without the need to remove the coating layer. In uncoated lamps RBS can measure Hg uptake in soda lime glass within the first hour of operation. We have used RBS to characterize the effectiveness of coating layers in reducing interaction between Hg and the glass lamp envelope. Results from actual fluorescent lamps will be compared with quartz and soda lime glass wafers implanted with known amounts of mercury.

10:00am **AS-MoM6 Investigation of the Tribological System of Roller Bearings with TOF-SIMS**, *U. Gunst*, *D. Lipinsky*, Westfälische Wilhelms-Universität Münster, Germany; *W.-R. Zabel*, *G. Poll*, Universität Hannover, Germany; *H.F. Arlinghaus*, Westfälische Wilhelms-Universität Münster, Germany

Tribology is a term describing an important and often complicated set of topics involving friction, lubrication, and wear. The surface characterization of tribological systems is of high importance to enhance their lifetime and to reduce economical loss. We have used time-of-flight secondary ion mass spectrometry (TOF-SIMS) in order to characterize the composition of tribosurfaces and of tribointerfaces of high speed rolling element bearings. Different TOF-SIMS methods (static TOF-SIMS, imaging, and depth profiling) were applied to investigate the elemental and molecular surface compositions as a result of interacting surfaces, friction, lubrication, and wear. Using static TOF-SIMS, semi-fluid lubricants, additives, the bearing steel, and the cage material were analyzed to establish reference information. The greases and roller bearing steel surfaces were investigated again after performing tribological test runs with real bearings under almost real application conditions. For these tests the addition of the lubricants was varied using different primary, ashfree antioxidants. We used TOF-SIMS imaging for the characterization of these tribosurfaces within the race way of angular contact ball bearings. The depth composition of tribological boundary layers was analyzed by performing TOF-SIMS dual beam depth profiling on the top of roller bearing balls, as well as in the bearing race ways. Significant elemental and molecular species were found for lateral and depth distributions of different tribological layer regions - giving correlations to tribological models and interaction mechanisms.

10:20am **AS-MoM7 Interfacial Analysis between Amorphous Carbon Films and Glass by XPS and Improvement of Adhesion Strength at the Interface by Plasma Treatment**, *S. Takeda*, *S. Suzuki*, Asahi Glass Co., Ltd, Japan

Amorphous carbon (a-C) films are widely applied in data storage and microelectronic industries because of their unique properties such as excellent hardness, good wear resistance, low friction coefficient, good chemical resistance and high electrical and thermal conductivities etc. However, in case of deposition of the a-C films onto glass, adhesion strength of the films to glass substrate is very poor and the film is easily delaminated at the interface between the film and glass. This is a serious problem for practical applications. Namely, improvement of the adhesion strength is a key issue to apply the a-C films to practical products. In order to overcome this problem, we investigated the effects of plasma treatment in Ar, N₂ and O₂ prior to the film deposition on the adhesion strength of the films to glass substrate. In the presentation, we report a major factor governing the adhesion strength based on the interfacial analysis between the a-C films and glass by X-ray photoelectron spectroscopy.

10:40am **AS-MoM8 Determination of SiGe Film Composition and Thickness by Combined AES and Multiple-Voltage X-ray Emission Analysis**, *J.T. Armstrong*, *S.A. Wight*, *R.B. Marinenko*, *D.S. Simons*, *E.B. Steel*, National Institute of Standards and Technology

SiGe epitaxially grown on Si is used for bandgap-engineered devices with significant potential in a variety of microelectronic products. The composition of SiGe layers is often determined by RBS; however, the analytical accuracy is limited to ~5-10%, in part due to the lack of suitable standards. We are working on development of higher accuracy analytical procedures to characterize SiGe films being considered as NIST reference materials (50-150 nm, 3-40 atom % Ge, grown on Si substrates). We use a combination of Auger electron spectroscopy, multiple voltage x-ray emission analysis, and SIMS to determine their homogeneity, thickness and composition. Results are compared to measurements made on a series of bulk SiGe alloys also being investigated as possible NIST reference materials. The new generation of field emission scanning Auger microprobes (FE-SAM) provides superior capabilities for this type of analysis. With our newly installed FE-SAM, we are able to simultaneously perform Auger electron spectroscopy and high precision and accuracy EDS

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x-ray analysis at beam energies ranging from <1 to 25 keV. Using low voltage EDS analysis (2-4 keV) (augmented by the lack of contamination enabled by UHV and incorporating our newly refined correction procedures) we are able to determine the film compositions to better than 2% relative. By multiple higher voltage x-ray analysis (5-25 keV) on the FEASAM and electron microprobe, we are able to determine the lateral homogeneity and thickness. By AES and SIMS we are able to determine the in-depth homogeneity of the films and separately estimate their thickness. Preliminary results show good agreement among these measurements.

11:00am AS-MoM9 Carbon Gold Sulfide by 13.56 MHz Plasma CVD and Sputtering Process, *M.A. Kashem, S. Morita*, Nagoya University, Japan

Co-operation process of plasma CVD and sputtering is a well-known technique to fabricate metal containing carbonaceous film, however the metal was mixed in the film with polycrystalline structure at content more than a few atomic %.¹ CH₄ and SF₆ mixture gas plasma induced a unique reaction of HF dissociation and carbon sulfide could be synthesized.² A new carbon gold sulfide film was formed with using CH₄, SF₆ and Ar mixture gas plasma CVD and gold plate discharge electrode. The process was observed and discussed with using a mass spectroscopy. The gold atom was observed to distribute uniformly caused on chemical bond with carbon and sulfur. The carbon gold sulfide structure was confirmed by x-ray diffraction, XPS analysis and refractive index measurement on the effect of thermal treatment at 200 °C. The chemically bonded carbon gold sulfide suggested to be conductive. Therefore, the density of carbon gold sulfide molecular group was observed to affect on a dielectric and conductive property.¹ L. Marutinu, Solar Energy Materials 15, p.21 (1987).² M. Matsushita, Md. Zarid. Bin Harum, Md. Abul Kashem and S. Morita; J. Photopolym. Sci. and Tech., 12 (1) (1999) pp.11-14.

11:20am AS-MoM10 Thickness, Dose and Distribution Measurements of Silicon Oxynitride Ultra-thin Films, *R.K. Champaneria, P. Mack, R.G. White, J. Wolstenholme*, Thermo Electron, UK

The continuing requirement for smaller equivalent oxide thickness (EOT) for transistor gate dielectrics has lead to the introduction of new materials with higher dielectric constants than silicon dioxide (high-k dielectrics). At present, silicon oxynitride is an important material for this application. X-ray photoelectron spectroscopy (XPS) is a well-known surface analytical technique. It can provide quantitative information, not only about chemical elements but also their chemical state. The information depth of the technique varies with the material under investigation but is in the region of 5-10 nm for materials commonly encountered in semiconductor device fabrication. This information depth can be controlled by means of the angle at which the photoelectrons are collected (angle resolved XPS or ARXPS) and, by collecting the signal at a number of angles, it is possible to generate a concentration depth profile. Since no material is removed in the generation of the concentration profile, the method is essentially non-destructive. Data will be shown to illustrate how ARXPS can provide accurate and precise measurements of thickness and nitrogen dose in oxynitrides. It will be shown that XPS measurements at a single angle cannot provide accurate measurements of the dose. Using line scans or maps, the uniformity of thickness and dose across a wafer can be measured. ARXPS data can also be used to reconstruct concentration depth profiles. These profiles reveal both the total dose and the distribution of nitrogen in each of its chemical states. It will be shown that methods of profile generation involving sputtering can produce misleading results.

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Nanotube and Nanoparticle Characterization

Moderator: M.C. Burrell, GE Global Research

2:00pm AS-MoA1 Vibrational Behavior of Adsorbed CO@sub 2@ on the Interior and Exterior Surfaces of Carbon Nanotubes: An Experimental and First Principles Study, W.-L. Yim, O. Byl, P. Kondratyuk, J.K. Johnson, J.T. Yates, Jr., University of Pittsburgh

We have used CO@sub 2@ as a probe for the adsorption sites on single-walled carbon nanotubes (SWNTs). CO@sub 2@(g) shows an intense infrared band at 2349 cm@super -1@, due to the asymmetric CO@sub 2@ stretching mode. When CO@sub 2@ is adsorbed on (10,10) nanotube surfaces, this mode should be red shifted to a lower vibrational frequency. We measured the infrared spectrum of CO@sub 2@ adsorbed on SWNTs and have observed absorption peaks at 2341 cm@super -1@ and 2329 cm@super -1@. After ozone treatment and annealing in vacuum to 823 K, CO@sub 2@ adsorption causes the mode at 2329 cm@super -1@ to increase dramatically in intensity, with the peak at 2341 cm@super -1@ less affected. We have performed density functional calculations using the local density approximation on (10,10) SWNTs, with CO@sub 2@ adsorbed on interior, exterior, groove, and interstitial sites of bundles of the nanotubes. The CO@sub 2@ in the groove site and in the nanotube interior exhibit vibrational red shifts of 20.9 cm@super -1@ and 23.2 cm@super -1@, respectively, for the asymmetric stretching mode. This agrees very well with the experimental results for the larger shift. The CO@sub 2@ on the nanotube exterior has a theoretical red shift of 14.8 cm@super -1@ from the gas phase CO@sub 2@ mode, which may contribute to the peak at 2341 cm@super -1@ in the experiments. We have monitored the replacement of CO@sub 2@ by Xe through a series of co-adsorption experiments. Xe selectively replaces the CO@sub 2@ species giving the mode at 2329 cm@super -1@ and assigned to CO@sub 2@ bound inside the nanotubes. Thus, both experiments and simulations indicate that the more red-shifted absorption peak is due to CO@sub 2@ adsorbed on the inside and possibly the groove sites of the SWNT bundles. This work was supported by the Army Research Office.

2:20pm AS-MoA2 Adsorption and Dimerization of NO Inside of Single Walled Carbon Nanotubes - An Infrared Spectroscopic Study, P. Kondratyuk, O. Byl, J.T. Yates, Jr., University of Pittsburgh

The physical adsorption of NO on purified (10,10) single walled carbon nanotubes was investigated at low temperatures by means of transmission infrared spectroscopy. Ozone treatment followed by annealing was used as a method of opening the entry ports for adsorption into the interior of the nanotubes. The IR spectra show that NO which is adsorbed inside of nanotubes exists exclusively in its dimer form, with no infrared bands of the monomer visible at a sensitivity level of 5 mole % NO. The internally adsorbed NO dimer species observed is cis-(NO)@sub 2@ with $\nu_{\text{sub 1@}}(\text{symmetric}) = 1853 \text{ cm@super -1@}$ and $\nu_{\text{sub 5@}}(\text{asymmetric}) = 1754 \text{ cm@super -1@}$. Introduction of Xe into the system leads to selective displacement of the internally-bound cis-(NO)@sub 2@ dimer. A large spectroscopic red shift of the symmetric [-0.80%] and the asymmetric [-1.96%] modes for cis-(NO)@sub 2@ adsorbed inside of nanotubes (relative to gas phase cis-(NO)@sub 2@) points to the strong interaction of the dimer with the nanotube interior. The enthalpy of dissociation of the adsorbed dimer molecule is $15.1 \pm 0.7 \text{ kJ/mol}$.

2:40pm AS-MoA3 Adsorption of CF@sub 4@ on Opened Single Walled Carbon Nanotubes, O. Byl, P. Kondratyuk, L. Chen, J.K. Johnson, J.T. Yates, Jr., University of Pittsburgh

Single walled carbon nanotubes are currently the subject of intensive studies because of their potential application as sorbents. This is due to the deep potential energy well for adsorption inside of the nanotube. To make accessible the interior of the nanotube O@sub 3@ was used as an oxidizer to attack the strained endcaps and also defect sites, causing local oxidation of carbon atoms there. The ozonolysis was followed by annealing in vacuum to decompose carbonyl functionalities formed during the ozone treatment. Infrared spectroscopy has been used to make the first experimental discrimination between molecules bound by physisorption on the exterior surface of carbon single walled nanotubes (SWNTs) and molecules bound in the interior. In addition, the selective displacement of the internally-bound molecules has been observed as a second adsorbate is added. SWNTs were opened by oxidative treatment with O@sub 3@ at

room temperature, followed by heating in vacuum to 873 K. It was found that at 133 K and 0.033 Torr, CF@sub 4@ adsorbs on closed SWNTs exhibiting its $\nu_{\text{sub 3@}}$ asymmetric stretching mode at $1267 \text{ cm@super -1@}$ (redshift = -15 cm@super -1@). Adsorption on the nanotube exterior is accompanied by adsorption in the interior in the case of opened SWNTs. Internally-bound CF@sub 4@ exhibits its $\nu_{\text{sub 3@}}$ mode at $1247 \text{ cm@super -1@}$ (redshift = -35 cm@super -1@). It was shown that at 133 K, Xe preferentially displaces internally-bound CF@sub 4@ species, and this counter-intuitive observation was confirmed by molecular simulations. The pseudo-one-dimensional confinement of CF@sub 4@ inside of (10,10) single walled carbon nanotubes does not result in the production of the splitting caused by transition dipole - transition dipole interaction which is observed in 3D ensembles of CF@sub 4@.

3:00pm AS-MoA4 Sidewall Chemistry of Carbon Nanotubes Investigated by STM, K.F. Kelly, Rice University

There is a great deal of interest in understanding and controlling the chemistry of carbon nanotube sidewall functionalization. Enhanced solubility, improved formation of composite materials, controlled modification of the electronic structure, and increased hydrogen storage capacity are a few of the applications that this technology may impact. In this talk we will present scanning tunneling microscope studies of partially and fully fluorinated single-walled carbon nanotubes. In addition, we have imaged carbon nanotube sidewalls modified by various solution chemistry methods. Differences in electronic structure and surface coverage produced by each method will be discussed.

3:20pm AS-MoA5 Iron-Oxide Nanoparticle Stability in an Ion Beam, K.H. Pecher, D.R. Baer, M.H. Engelhard, Pacific Northwest National Laboratory

The immense interest in nano-structured materials necessarily leads to application of various methods of surface analysis to examine the composition, chemical state and other properties of such materials. There are a variety of reasons why the chemical properties of nanoparticles may differ from bulk versions of similar material. We have been examining various types of iron metal and oxide nanoparticles to understand their chemical behavior. During the course of study 30 nm diameter iron oxide particles distributed on a silicon wafer or a gold coated wafer were exposed to 2 kV ions. In comparison to a 30 nm thick iron oxide film, the nanoparticles were significantly altered. Particles suspended on Au were significantly reduced while particles distributed on the uncoated wafer rapidly formed an iron silicide. Further studies show that aggregates of nanoparticles do not show the same reduction. The stability of nanostructures when subjected to various types of analysis may be a significant complication to the study of these interesting materials.

3:40pm AS-MoA6 Scanning Tunneling Spectroscopy of Boron Nitride Nanotubes; Evidence for a Giant Stark Effect, S. Aloni, University of California at Berkeley and Lawrence Berkeley National Laboratory; *M. Ishigami,* University of California at Berkeley; *A. Zettl,* University of California at Berkeley and Lawrence Berkeley National Laboratory

The Electronic properties of double-walled boron nitride nanotubes BNNT's were studied by scanning tunneling microscopy and spectroscopy at 7K. High resolution topographs of the tubes reveal information about the hexagonal boron nitride lattice as well as information about interlayer coupling between inner and outer tube. Tunneling spectra are also strongly dependent on the electronic coupling between the tube and the substrate. When the tube is well coupled to the substrate the spectra clearly show manifestation of a one dimensionality of the electronic structure and band gaps of 3.5eV. However, weakly coupled tubes display significantly higher apparent band gaps of 7-9.5 eV, indicating that the applied electric field is not fully applied across the tunneling gap between the STM tip and the tube. Simple analysis of the current-distance spectra shows that the actual BNNT bandgap is significantly smaller (3-5 eV) and is attributed to a second tunneling junction present between the tube and the under-laying substrate. Unlike their carbon analogues, BNNT are expected to be semiconducting with a chirality independent band gap of 5-5.5eV. We explain the low measured band gap values by a tip induced giant Stark effect, where the band gap is narrowed due to the high electric field as predicted in recent theoretical calculations by S.Louie et al.

4:00pm AS-MoA7 Size Dependency of Structural, Optical, and Photocatalytic Properties of TiO@sub 2@ Nanoparticles, W. Li, S.I. Shah, S. Lin, C. Ni, C.-P. Huang, University of Delaware

Polycrystalline TiO₂ anatase nanoparticles with different average sizes (12, 17, 23 nm) were synthesized by metallorganic chemical vapor deposition (MOCVD). The particle sizes were determined by x-ray diffraction and

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transmission electron microscopy. The specific surface areas varied between 50 and 150 m²/gm, as measured by Brunauer-Emmett-Teller (BET) method. The size effects on the thermodynamic stability of TiO₂ was analyzed by annealing samples in the temperature range of 700 to 800 oC. Only anatase to rutile phase transformation occurred. The transformation rate was accelerated with the decrease of initial particle size. The activation energy was calculated from the XRD data. The activation energy decreased from 298.85 to 180.28 kJ/mol as the initial anatase particle size decreased from 23 to 12 nm. Photoabsorption measurements showed a red shift of the absorption edges with the decrease in the particle size down to 17 nm. Below this particle size, a blue shift was observed. Photodegradation of 2-chlorophenol solutions under ultraviolet irradiation showed 17 nm sample had the highest photoreactivity. This result will be discussed on the basis of size related difference of light absorption efficiency, active surface area, and lifetime of charge carriers.

4:20pm **AS-MoA8 Determination of the Fermi Level of Isolated Single-Walled Carbon Nanotubes in Solution**, *K. Murakoshi*, Hokkaido University, Japan

Single-walled carbon nanotubes (SWNT) should be among the best candidates for ultra-small functional units in ultra-sensitive, low-energy consumption nano-devices. Several characteristics of the electronic band structure of individual SWNT have been obtained successfully employing recently developed experimental techniques in confocal micro Raman spectroscopy, scanning tunneling microscopy and fluorescence methodology. In addition to band profiles, information regarding absolute potential of energy levels of the states is known to be essential to nano-device fabrication. Several estimations of energy levels from measurements of work function were attempted in vacuums and in electrolyte solution; however, all of these measurements utilized bulk bundle SWNT, which display certain distributions with respect to size. The diameter-dependent absolute potential of individual tubes has never been observed experimentally. The present report reveals that the energy position of the Fermi level of individual SWNT relative to the vacuum level depends on tube diameter based on measurements of resonance Raman intensity of individual SWNT under electrochemical potential control. Absolute potential of the Fermi level was found to be extremely sensitive to tube diameter. Structural dependence of metallic tubes is larger than that of semiconducting tubes. The values obtained can provide absolute potential maps of single SWNT at interface.

4:40pm **AS-MoA9 Band Modulation in Various Nanopeapods and Its Origin**, *J. Lee, H. Kim*, Seoul National University, Korea; *S.-J. Kahng*, Korea University, Korea; *J. Ihm*, Seoul National University, Korea; *H. Shinohara*, Nagoya University, Japan; *Y. Kuk*, Seoul National University, Korea

Recent studies show interesting electronic properties of carbon nanotubes with various metallofullerenes. We have performed scanning tunnelling microscopy and spectroscopy study on these peapods. Two surprising characters were found: 1) large magnitude of the bandgap modulation (as large as ~1eV in Gd@sub 2@C@sub 92@ peapods and ~0.3eV in GdC@sub 82@ peapods) and 2) multiple oscillation of the conduction band edge in the position dependent spectroscopy near a defect. Our theoretical simulation results partly describe the main features in the experimental data. The modulation of band is caused by derived states from states of nanotube and metallofullerene. The conduction band oscillation was explained by many body screening effect around a defect. The observation of multiple fringe patterns near a potential barrier was predicted in the STM theory of Luttinger liquid near a perfect reflecting boundary, which expected a set of infinitely extending hyperbolars in the dI/dV(X,V) spectra. In the case of metallofullerene peapod, however, the finite barrier potential can result in curvilinear subbands surrounding the scattering potential. The current results imply that the transport properties of peapods may be dominated by the extent and strength of the scattering potential associated with the electronic structure of the inserted metallofullerenes. The recent transport measurement also supports our observation and calculation. A more detailed understanding of the phenomenon may require a many-body electron screening theory with the pseudo-2D geometry and external potential.

@FootnoteText@ @footnote 1@ Jinhwan Lee, H. Kim, S.-J. Kahng, G. Kim, Y.-W. Son, J. Ihm, H. Kato, Z. W. Wang, T. Okazaki, H. Shinohara, and Young Kuk, Nature 415, 1005 (2002). @footnote 2@ Sebastian Eggert, Phys. Rev. Lett. 84, 4413 (2000) @footnote 3@ P.-W. Chiu, G. Gu, G.-T. Kim, G. Philipp, S. Roth, S.F. Fang, and S. Yang, Appl. Phys. Lett. 79(23), 3845-3847 (2001).

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Room 324/325 - Session AS-TuM

Image Analysis and Polymer Characterization

Moderator: F.A. Stevie, North Carolina State University

8:40am **AS-TuM2 Advances in Chemical Imaging: NanoSAM and NanoESCA**, *J. Westermann, G. Schaefer, D. Funnemann, M. Maier*, Omicron NanoTechnology, GmbH, Germany

Electron spectroscopy has been a proven tool for scientific applications for decades. Challenging new applications are emerging from the fields of semiconductor and nanotechnology research and a key issue for these areas is the non-destructive imaging of sensitive structures with nanoscale dimensions. Characterization of their chemical composition and electrical properties goes hand in hand with this. We report on the development of two novel electron microscopes for chemical imaging that meet these requirements, especially for lateral image resolution in the nanoscale range. I. NanoSAM We present electron optical concepts and first results of a truly UHV compatible SEM column designed to meet the requirements for high-resolution with high beam currents. Performance checks on nanostructured samples demonstrate spot sizes below 3 nm at 15 keV beam energy and better than 5 nm at 3 keV, with sample currents being suitable for Auger electron analysis. Latest static Auger and SAM results, demonstrating the outstanding spatial resolution, will be shown. II. NanoESCA We present a parallel imaging electron microscope with an integrated high-resolution energy filter for Imaging XPS. It consists of a Photo Emission Electron Microscope (PEEM) with a large angular acceptance and an aberration corrected energy filter. The microscope allows for imaging with chemical contrast (Imaging ESCA) by energy filtering of photoelectron images. The analyzed energy of the photoelectron images ranges from threshold photoemission to 1600 eV. The instrument has been characterized with laboratory and synchrotron excitation sources. The spatial resolution limit measured so far in imaging ESCA mode is about 150 nm. The measured energy resolution follows the theoretical calculations. We show XPS spectra and energy filtered image series (video sequences) of: AlGaAs heterostructures, microstructured Au/Si and Ag/Ta samples.

9:00am **AS-TuM3 Correlation of XPS and AFM Images for Polymer Blends**, *J. Farrar, K. Artyushkova, J.E. Fulghum*, University of New Mexico; *F. Xu, N. Bantan, J. Khan*, Kent State University

Multi-technique analysis of heterogeneous polymer samples, based on AFM and XPS imaging, will provide a more complete picture of the sample under study than either technique alone. AFM provides both topographical and phase contrast information on the nanometer scale, but no chemical information is provided. Imaging XPS provides elemental and chemical information on the micron scale. A method to chemically identify the observed phases in AFM through correlation with quantitative XPS imaging will be discussed. Correlating the data from both techniques involves resizing, image alignment, resolution matching, and classification methods. The approach will be applied to a patterned polymer surface of known properties for validation and then to heterogeneous polymer blends of polystyrene/polybutadiene for phase identification. This project represents one aspect of the Active Knowledge Mesh Model (AKM) that is currently under development in our laboratories. AKM is a comprehensive image analysis system that integrates data from different techniques into a realistic three-dimensional model, visualizing structure and morphology, in multicomponent heterogeneous samples. This work has been partially supported by NSF ALCOM (DMR89-20147), NSF CHE-0113724, NSF IGERT CORE and UNM.

9:20am **AS-TuM4 XPS and Confocal Microscopy Data Fusion for Polymer Characterization**, *K. Artyushkova, J.E. Fulghum, J. Fenton, J. Farrar*, The University of New Mexico; *J. Khan, F. Xu, N. Bantan*, Kent State University

Advances in materials development require a three-dimensional characterization of complex polymeric samples in terms of both chemical structure and morphology over feature sizes ranging from nanometers to millimeters. Correlating information from multiple techniques is one method for the development of a comprehensive 'picture' of the material under study. New opportunities for multi-technique correlations arise from the improved spatial resolution and decreased acquisition times now available in a variety of imaging methods. Imaging XPS and confocal microscopy (CM) are complementary techniques that, in combination, allow for the visualization of the internal structure of heterogeneous

polymer samples. Quantitative chemical information that is readily available from the surface sensitive XPS images and spectra will be used to extract quantitative data from confocal images, which are acquired from different depth levels throughout the sample. The XPS and CM data sets can then be 'fused' to provide a surface-to-bulk visualization of changes in polymer chemistry. This work has been partially supported by NSF CHE-0113724 and NSF IGERT CORE program.

9:40am **AS-TuM5 Solvent Enhanced Surface Modification of Polymers Accompanying AFM Tip Induced Mechanical Stresses**, *F. Stevens, R. Leach, J.T. Dickinson*, Washington State University

The response of thin polymer films and bulk surfaces to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by an AFM tip in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "protrusion" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one observes a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have made a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface of several molecular weights in four solvents with dramatic differences in response. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by AFM. Extending this work, we have added temperature as a parameter, performing the tip stimulation at temperatures from 0 - 120 C. Major changes in the structures formed occur at higher temperatures due to increased solvent mobility and polymer mechanical properties with temperature.

10:00am **AS-TuM6 SF5+ Ion Beam Damage of Poly(Acrylates) Studied using Time of Flight Secondary Ion Mass Spectrometry**, *M.S. Wagner, G. Gillen*, National Institute of Standards and Technology

Recent advancements in instrumentation for Secondary Ion Mass Spectrometry (SIMS) have focused on the development of polyatomic primary ion sources. Polyatomic ions have been shown to increase the secondary ion yields of molecular ions from organic materials when compared with monoatomic ions of similar mass. Furthermore, some polymer films, notably poly(methyl methacrylate) and poly(ethylene glycol), display the unusual characteristic of maintaining their characteristic molecular ion signals after extended polyatomic ion bombardment. This study focuses on the effect of the chemical structure of the polymer on its stability under extended SF5+ ion bombardment. The damage of spin cast polymer films by 5 keV SF5+ was studied using positive and negative ion static Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). A class of poly(acrylate) polymers with systematic changes to the monomer structure were investigated to determine the effects of polymer structure on the stability of their characteristic ion signals under 5 kV SF5+ bombardment in the ion dose range from 2.5 x 10@super 13@ - 5 x 10@super 14@ SF5+ ions/cm@super 2@. Preliminary results have shown that poly(methacrylic acid) and poly(methyl methacrylate) were stable under extended SF5+ bombardment while poly(methyl acrylate) was not, suggesting a role for the methyl group on the central carbon in the stabilization of the polymers under SF5+ bombardment. Monte Carlo calculations using the SRIM software@footnote 1@ show that the penetration depths of fluorine and sulfur ions in these polymers were the same despite the different damage characteristics, highlighting the importance of the chemical structure of the polymer on its stability under polyatomic ion bombardment. This study describes the breadth of applicability of SF5+ sputtering to the depth profiling of polymer films. @FootnoteText@ @footnote 1@ More information on this program can be found at <http://www.srim.org>.

10:20am **AS-TuM7 Time-of-Flight Secondary Ion Mass Spectrometry of Ordered Polymeric Monolayers: Effect on Tertiary Structures**, *J.A. Gardella, Jr., R. Rey-Santos*, State University of New York at Buffalo

The study of polymer surface structures has become an important topic in surface chemistry. Poly(dimethylsiloxane) (PDMS) plays very important roles in biological and pharmaceutical applications. A similar study of poly(methylmethacrylate) published by Nowak et al in Analytical Chemistry in 2000 was used as a model. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is one of the most powerful techniques for

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polymer study. TOF-SIMS was used to study the fragmentation mechanism of this polymer. Using a statistical chain breaking model of PDMS helped us to understand the fragmentation pattern obtained in the spectra. The Langmuir-Blodgett (LB) technique helps us to prepare a molecular monolayer at the air/water interface. The LB technique was used to prepare well-ordered monolayers. Reflection Absorption Fourier Transform Infrared Spectrophotometry (RA-FTIR) is an ideal technique for surface study to obtain information about molecular structures. It has been used to compare results from amorphous, solution cast films to that from ordered, LB films of PDMS. An ion formation mechanism for PDMS was investigated to get information of the long-range forces between polymer chains.

10:40am **AS-TuM8 Grazing Incident X-ray Diffraction Study of Poly(alkylthiophene) Thin Films on Various Substrates**, *M. Morita, T. Koga, H. Yakabe, S. Sasaki*, Kyushu University, Japan; *O. Sakata*, JASRI, Japan; *A. Takahara*, Kyushu University, Japan

The crystalline aggregation states of organic semiconductor molecules in thin films might play an important role in the performance of organic semiconductors. The purpose of this study is to reveal the crystalline orientation and crystallinity of spin-coated poly(3-hexylthiophene)[P3HT] on Si-wafer substrate at the near-surface region and internal phase. The surface crystalline states of P3HT thin film were studied with synchrotron radiation in-plane grazing incidence x-ray diffraction GIXD. Surface modification of Si-wafer with perfluorohexylethyltrimethoxysilane prior to P3HT coating resulted in the preferential orientation with the alkyl side chains normal to the substrate surface. In contrast, the surface modification of Si-wafer with vacuum ultraviolet(VUV)-ray with wave length of 172nm or n-octadecyltrimethoxysilane resulted in the orientation with the alkyl side chains parallel to the substrate.

11:00am **AS-TuM9 Study of Water-Induced Reorganization of Amphiphilic Graft Copolymers Containing Poly(2-hydroxyethyl methacrylate) and Polydimethylsiloxane by Angle-dependent X-ray Photoelectron Spectroscopy**, *L. Chen*, State University of New York at Buffalo; *A.P. van Bavel*, Eindhoven University of Technology, The Netherlands; *J.A. Gardella*, State University of New York at Buffalo

The free air surface composition and water-induced reorganization of a series of amphiphilic graft copolymers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) [poly(HEMA)] backbones and hydrophobic poly(dimethylsiloxane) (PDMS) side chains prepared by both photoinduced-radical and anionic polymerization techniques were studied by angle-dependent X-ray Photoelectron Spectroscopy (XPS). Copolymers with broad molecular weight distributions (MWD; e. g. Mw/Mn = 3.0) were prepared by the radical copolymerization technique. Copolymers with narrow MWD (e. g. Mw/Mn = 1.1) were prepared by the anionic copolymerization technique. The free air surface composition of copolymers was studied as a function of MWD, PDMS bulk content and PDMS graft length. It was found that anionically prepared copolymers with narrow MWD have higher PDMS surface concentration than radically prepared copolymers with broad MWD. PDMS surface concentration increased with increasing PDMS bulk content. For a given PDMS bulk content, a longer PDMS graft chain gave a surface richer in siloxane. The water-induced reorganization of copolymers was studied as a function of MWD, PDMS graft length and water exposure time. The dry films were exposed to water (hydration) and then frozen in a nitrogen gas purge to preserve the surface composition during XPS analysis. The XPS results showed both MWD and PDMS graft length influenced the extent of the graft chain reorganization at the surface.

11:20am **AS-TuM10 The Role of Polymer Architecture and Environmental Humidity on the Interfacial Conformation and Properties of Surface-adsorbed Poly(L-lysine)-graft-poly(ethylene Glycol) Co-polymer**, *F. Assi, S. Pasche, L. Feuz, N.D. Spencer, M. Textor*, ETH Zurich, Switzerland

The development of protein-resistant surfaces is of central interest in the context of biosensor chip development and for the design of medical implants in contact with blood. Self-organized films of PEG based copolymers on different oxide surfaces are one system that has been investigated by a variety of surface characterization techniques in order to establish systematic correlations between the polymer composition/structure, interface architecture and interaction with protein-based biological media. A class of co-polymeric molecules of special interest is based on a poly(L-lysine) backbone, charged positively due to the presence of protonated amine groups at a neutral pH, and grafted with poly(ethylene glycol) side chains (short: PLL-g-PEG). Although the protein-resistant properties of these films have already been demonstrated, little is known about the effect of the co-polymer interfacial architecture on the

resulting protein resistance. One of the most important factors turns out to be the polymer conformation in the adsorbed state, which depends not only on the polymer architecture but also on the environment the polymer, is exposed to. We report results that elucidate the surface conformation of PLL-g-PEG of different molecular architecture at various humidity levels in air as well as in contact with aqueous solutions, studied by means of atomic force microscopy (AFM, for the polymer conformation and adhesion properties) and ellipsometry (ELM, for the layer thickness). AFM force-distance measurements in compression between a 5- μm SiO₂@sub 2@ sphere and a PLL-g-PEG-coated substrate showed a good correlation with the architecture of the polymer. Furthermore, tensile-mode (pull-off) AFM studies were used to quantify the adhesion strength level of the polymeric molecules at oxide surfaces. The experimental results for different polymers were finally compared to the results of self-consistent field calculations.

11:40am **AS-TuM11 Ultra-fast Laser Ablation as a Facilitator for Depth-dependant Characterization of High Pigment Volume Concentration Organic Coatings**, *L.T. Keene, C.R. Clayton, G.P. Halada, T. Fiero*, State University of New York at Stony Brook

The strong dielectric nature of most organic coatings, particularly those used on an industrial scale, presents the scientific investigator considering a depth-profiling approach to chemical characterization of such organic coatings with a serious challenge. The ultra-fast optical phenomenon of femtosecond laser ablation presents one possible solution to such a problem. An apparent athermal, non-selective ablation process becomes possible when the pulse temporal scale reaches the femtosecond (10⁻¹⁵ s) level. This remarkable property of femtosecond-class lasers enables the multi-layer removal of organic/inorganic composite coatings for the purpose of chemical characterization as a function of coating depth. If proven experimentally, this capability becomes attractive when considering the depth-analysis of materials that demonstrate either strong dielectric properties (and, hence, resist depth profiling via traditional charged particle beam methods) or are chemically inhomogeneous in nature (which generally cause problems such as selective sputtering). This talk will focus on the experimental use of ultra-fast laser ablation for the facilitation of depth-profiling high solids organic coatings with particular emphasis placed on military application two-component solvent-based polyurethane coatings containing a variety of inorganic pigments and fillers. The high dielectric and chemically inhomogeneous natures of these coatings pose a demanding application for uniform laser removal without chemically modifying the host material. Cross-sectional analysis of the materials via Scanning Electron Microscopy (SEM) / Energy Dispersive Analysis of X-rays (EDS) will be shown. Ablation of the aforementioned materials was conducted both in atmosphere as well as high vacuum. Chemical modification of host material due to the ablation process will be discussed via the results of Fourier Transform Infrared Spectroscopic analysis of ablated material before, and after, ablation. Morphological features of ablated regions collected via high-resolution scanning confocal profilometry as a function of the processing parameters, and how these features limit the removal depth resolution, will be shown. S. McKnight, J. Beatty, Mechanisms of Military Coatings Degradation, ARL Weapons & Materials Directorate, (1999) 1. C.R. Hegedus, et. al., "A Review of Organic Coating Technology for U.S. Naval Aircraft," Journal of Coatings Technology, Vol. 61, No. 778, pp 31-42, (1989) 3. L. Keene, G. Halada, C. Clayton, S. McKnight, W. Kosik, "Novel Techniques for the Investigation of Long-term Photodegradation of Multi-layer Polymer Coatings," in State-Of-The-Art Application of Surface and Interface Analysis Methods, The Electrochemical Society Proceeding Series, Pennington, NJ, (199th Electrochemical Society Meeting; Washington D.C.) (2001) 4. A.A. Serafetinides, M.I. Makropoulou, C.D. Skordoulis, A.K. Kar Appl. Surf. Sci. 42-56 (2001) 180

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Room 324/325 - Session AS+BI-TuA

Biomaterials Characterization

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

2:00pm AS+BI-TuA1 Spatially Defined Immobilization of Biomolecules on Microstructured Polymer Substrate*, A. Hozumi, N. Shirahata, National Institute of Advanced Industrial Science and Technology, Japan; S. Asakura, A. Fuwa, Waseda University, Japan; Y. Yokogawa, T. Kameyama, National Institute of Advanced Industrial Science and Technology, Japan

The spatial arrangement of biomolecules on solid surfaces with artificial control in the micro-nanometer scale has attracted attention in biotechnical and biomedical applications. Here we report a simple method by which a number of biomolecules can be immobilized onto positions spatially defined in micrometer-scale. Our approach demonstrated here is based on the photodecomposition and hydrophilization of polymeric material using vacuum ultraviolet (VUV) light of 172 nm radiated from a Xe@sub 2@@super *@ excimer lamp. Each poly (methyl methacrylate) (PMMA) substrate was irradiated for 30 min at 10@super 3@ Pa with VUV light through a photomask contacting the PMMA surface. As confirmed by atomic force microscopy, after VUV-irradiation, microwell arrays composed of about 2 nm in diameter and 350 nm in depth were successfully formed on the PMMA substrates. Next, using such microstructured PMMA substrates, we demonstrated spatial arrangement of biomolecules. The microstructured sample was immersed into a solution containing antibodies labeled with fluorescence for 30 min. The antibodies were selectively adsorbed on the microwells in which the surfaces were photooxidized, while the surrounding regions where they were not unirradiated regions remained free of adsorption, as evidenced by fluorescence microscopy. This specific adsorption was probably due to the differences in chemical properties between the VUV-irradiated and unirradiated regions, as well as due to the geometrical effect. Indeed, according to water-contact angle measurements and X-ray photoelectron spectroscopy analysis, the VUV-irradiated PMMA surface became highly hydrophilic with its water-contact angle changing from 80Å...Å to 25Å...Å due to the formation of polar-functional groups, such as C=O and O-C=O, on the surface. Such chemically and geometrically defined microwells are expected to serve as spatially arranged active sites for the immobilization of a wide variety of biomolecules.)

2:40pm AS+BI-TuA3 Low-Temperature STM Manipulation of Single Bio Molecules, J.J. Benson, V. Iancu, A. Deshpande, S.-W. Hla, Ohio University, Athens

Single porphyrin molecules adsorbed on Cu(111) surface are investigated by using a variety of manipulation procedures and spectro/microscopy measurements with a low temperature UHV STM at 6 K. The tunneling I/V and dI/dV spectroscopy techniques are used to probe the electronic properties of the single molecules with atomic level precision. @footnote 1@ Mechanical stability of single molecules is also examined using 'lateral manipulation' techniques with the STM-tip. @footnote 2@ In this procedure, the STM-tip is brought very close to the molecule to increase tip-molecule interactions (approximately one angstrom from the molecule). Then the tip is moved across the surface. Due to the tip-molecule interaction, the molecule is pushed across the substrate to relocate it to specific surface sites. Detailed internal conformation changes of the molecule can be directly monitored through the corresponding STM-tip height signals during the lateral manipulation process. These combined STM manipulation/spectroscopy investigations elucidate detailed information about the electronics and mechanical properties of the porphyrin molecules at sub-nanometer level resolutions. @FootnoteText@@@footnote 1@F. Moresco et al, Phys. Rev. Lett. 86, 672-675, (2001). @footnote @@S.-W. Hla, K.-H. Rieder, Ann. Rev. Phys. Chem. 54, 307-330, (2003). .

3:00pm AS+BI-TuA4 Base-dependent Displacement of Thiolated DNA Films by Mercaptohexanol (MCH), H. Kimura-Suda, National Institute of Standards and Technology; D.Y. Petrovykh, University of Maryland & Naval Research Laboratory; L.J. Whitman, Naval Research Laboratory; M. Tarlov, National Institute of Standards and Technology

The immobilization of DNA on surfaces is the basis for DNA microarrays and many emerging nanotechnology applications. It has been demonstrated that the attachment of thiolated DNA probes to gold surfaces is an effective approach for construction of DNA-based sensors and diagnostics. One challenge with the use of thiolated DNA is reproducibly controlling the surface coverage and hybridization activity of adsorbed probes. A two-step

method, where first the gold substrate is exposed to a solution of thiol-modified single-stranded DNA (HS-DNA), followed by exposure to a solution of mercaptohexanol (MCH), is a common approach for controlling the coverage and orientation of DNA probes. In this protocol, MCH both passivates the surface against nonspecific adsorption of DNA targets and "activates" DNA probes by displacing adsorbed nucleotides from the gold surface. The MCH treatment also displaces DNA probes from the gold surface resulting in less steric hindrance for hybridization. Nonetheless, the displacement of thiolated DNA by MCH remains poorly understood. In this study, we focused on base-dependent displacement of HS-DNA films from gold upon MCH exposure. Self-assembled monolayers of thiolated homooligonucleotides [HS-(dA), HS-(dT), HS-(dC), HS-(dG)] on gold surfaces were produced and characterized before and after exposure to MCH with FTIR and XPS. Surprisingly, we find that the displacement of HS-DNA on gold by MCH is strongly base-dependent. For example, most HS-(dT) is removed or displaced, whereas most HS-(dC) remains on the surface. In this talk we will present a selectivity series for the base dependent displacement of homooligonucleotides by MCH and discuss the origin of this effect. We will demonstrate that base dependent displacement effects can account for dramatic variations in probe coverage for probes of different base composition.

3:20pm AS+BI-TuA5 Neuron Pathfinding and Surface Chemistry, Patterning and Reactions, T.P. Beebe, Jr., University of Delaware INVITED

Biomaterials interfaces are at the heart of new approaches to control cell-surface interactions, and modern surface analytical techniques can now provide molecular-scale information about surface modifications, coverages and patterning or relevant ligands and proteins. These approaches can inform our understanding of the relationship between surface chemistry, surface structure and biological function. Using the biomedical problem of repair to damaged central nervous system tissue as the motivation for biomaterials interface characterization and cell-surface interactions, we will present several approaches to surface modification and surface characterization in conjunction with cell-surface biophysical measurements. The tools for these studies are AFM, XPS, TOF-SIMS and fluorescence microscopy and labeling.

4:00pm AS+BI-TuA7 In-situ Spectroscopic Study of Thermal Phase Transition of Supported Hybrid Bilayer Membranes, C.S.-C. Yang, K.A. Briggman, J.C. Stephenson, L.J. Richter, National Institute of Standards and Technology

Hydrated phospholipid structures (Langmuir-Blodgett films, supported bilayers, vesicles, etc.) have been widely studied as model systems for biological membranes. We report a study of the thermal phase transitions of fully hydrated hybrid bilayer membranes, i.e. phospholipid monolayers self-assembled onto a Au surface previously modified by a self-assembled monolayer of octadecane thiol (ODT). Using Sum Frequency Generation, a non-destructive interface-sensitive nonlinear optical probe, the structure and conformation of both the ODT and phospholipid alkyl chains have been characterized as a function of temperature from 25 to 60 °C. There is very little change in the ODT alkyl chain order over the temperature range studied. There are significant changes in the lipid chain order that are attributed to the transition from the ordered gel phase to disordered fluid phase, allowing us to determine the phase transition temperatures of the two-dimensional lipid layer. The gel-fluid phase transitions for a series of saturated phospholipids in the hybrid bilayers are observed at ~ 10 °C higher temperatures than those in corresponding multilamellar vesicles.

4:20pm AS+BI-TuA8 Spectroscopic Quantification of Covalently Immobilized Oligonucleotides, A.V. Sapragin, C.W. Thomas, C.H. Patterson, M.S. Spector, Naval Research Laboratory

Quantitative determination of surface coverage, film thickness, and molecular orientation of DNA oligomers covalently attached to aminosilane monolayers has been obtained using complementary infrared and photoelectron studies. Spectral variations between the different nucleic acids are observed in surface immobilized oligomers for the first time. Carbodiimide condensation was used to covalently attach phosphorylated oligonucleotides to silanized aluminum substrates. Fourier-transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to characterize the surfaces after each modification step. Infrared reflection-absorption spectroscopy of covalently bound DNA provides orientational information. Surface density and layer thickness are extracted from XPS data. The surface density of immobilized DNA, 2-3Å—10¹³ molecules/cm², was found to depend on base composition. Comparison of antisymmetric to symmetric phosphate stretching band intensities in reflection-absorption spectra of immobilized DNA and

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transmission FTIR spectra of DNA in KBr pellet indicates that the sugar-phosphate backbone is predominantly oriented with the sugar-phosphate backbone lying parallel to the surface, in agreement with the 10-20 Å... DNA film thickness derived from XPS intensities.

4:40pm **AS+BI-TuA9 Photoionization for Trace Measurement of DNA on Surfaces**, *J.F. Moore, W.F. Calaway*, Argonne National Laboratory; *B.V. King*, University of Newcastle, Australia; *J.W. Lewellen, S.V. Milton, M.J. Pellin*, Argonne National Laboratory; *M. Petrvic*, Australian National University; *I.V. Vervovkin*, Argonne National Laboratory; *G.L. Woloschak*, Northwestern University

Recent developments in vacuum ultraviolet (VUV) lasers allow new photoionization techniques to be applied to surface and interface analysis problems. Single photon ionization of laser desorbed nucleosides and DNA was performed using a molecular F@SUB 2@ laser (wavelength 157 nm, pulse energy 8 mJ, pulse length 10 ns) and a tunable free electron laser (wavelength 120 - 265 nm, pulse energy 0.1 mJ, pulse length 300 fs). Results including detection limit and degree of fragmentation are compared for several systems including guanosine and single-stranded DNA of 10-30 base pair lengths. The tunability of the free electron laser to a wavelength just above the ionization potential of the analyte molecule can be used to enhance selectivity and sensitivity of the analysis. There are clear applications of this sensitive, selective, spatially resolving technique that is capable of identifying mutated or adducted DNA with little sample preparation. These uses will be elaborated on in the context of our results and plans for further technique development, and operational experience with the free electron laser. @FootnoteText@ This work is supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

5:00pm **AS+BI-TuA10 Utilization of Polyatomic Primary Ion Sources for Analysis of Drug Delivery Systems by Secondary Ion Mass Spectrometry (SIMS)**, *C.M. Mahoney, G. Gillen*, National Institute of Standards and Technology

The utilization of cluster primary ion beams in SIMS has become very popular in the last decade due to the increased secondary ion yields as compared to monoatomic sources.@footnote 1-4@ In particular the analysis of organic materials has gained considerable interest as these cluster primary ion beam sources (in particular SF@sub 5@@@super +@) have resulted in the enhancement of characteristic molecular secondary ion yields and have decreased the beam induced damage.@footnote 4@ Furthermore, the increased sputter rate with decreased beam damage has allowed for depth profiling in organic films and polymers for the first time with limited success.@footnote 4@ Here we explore the applicability of cluster SIMS in the analysis of various materials utilized in drug delivery. The effects of SF@sub 5@@@super +@ bombardment on molecular secondary ion yields will be explored in various biodegradable polymers (polylactic acid, polyglycolic acid and polycaprolactone) as well as several model drugs (theophylline, 4'-hydroxyacetanilide, amyloid probe). The enhancement in the sensitivity will then be applied to imaging applications where it will be shown that imaging with SF@sub 5@@@super +@ enhances the signal intensity as compared to Ar or Cs primary ions resulting in more sensitive imaging capabilities. This will be useful in many systems where the concentration of drug is very low (e.g. biological samples, ppb-ppm range). Dynamic SIMS analysis (utilizing SF@sub 5@@@super +@) of a series of polylactic acid films doped with varying concentrations of 4'-hydroxyacetanilide will also be discussed. @FootnoteText@ @footnote 1@ Kotter, F.; Benninghoven, A. *Applied Surface Science* 133 (1998) 47.@footnote 2@ Appelhans, A.D.; Delmore, J. *Anal. Chem.* 61 (1989) 1087.@footnote 3@ Gillen, G.; King, R.L.; Chmara, F. *J. Vac. Sci. Technol. A* 17(3) (1999) 845.@footnote 4@ Gillen, G.; Roberson, S.; *Rapid Commun. Mass Spectrom.* 12 (1998) 1303.

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Room 324/325 - Session AS-WeM

High-K Materials Interface Analysis

Moderator: H.G. Tompkins, Consultant

8:20am **AS-WeM1 Spectroscopic Characterization of High-k Dielectrics: Applications to Interface Electronic Structure and Stability Against Chemical Phase Separation**, *G. Lucovsky, Cristiano Krug*, North Carolina State University

INVITED

The lowest conduction band states of high-k transition metal and rare earth dielectrics are associated with localized anti-bonding d^* -states. Combining X-ray absorption spectroscopy, XAS, with vacuum ultra-violet spectroscopic ellipsometry, VUV SE, photoconductivity, PC, and internal photoemission, IPE, provides a way to study final state effects, in particular different d^* -states, and d^*-s^* -state splittings which can then be compared with ab initio calculations on small clusters. These studies provide important insights into empirical correlations between i) band gaps, and ii) conduction band offset energies with respect to crystalline silicon and atomic d-state energies which apply to both transition metal and rare earth dielectrics, including binary oxides, and silicate and aluminate alloys. These results provide important insights into optimization of silicate and aluminate alloys for minimum direct tunneling at a given equivalent oxide capacitance. Combining Fourier transform infra red spectroscopy, FTIR, and derivative X-ray photoelectron spectroscopy, XPS, with extended X-ray absorption fine structure spectroscopy, EXAFS, provides an unambiguous way to differentiate between chemical phase separation with different degrees of crystallization in Zr and Hf silicate gate dielectrics, and at their interfaces with Si. This is of importance for semiconductor device processing since chemical phase separation at 900C (1000C) in silicon dioxide-rich Zr (Hf) silicates not detectable by X-ray diffraction, XRD, reduces gate dielectric capacitance, and therefore can reduce current drive in field effect transistors, FETs.

9:00am **AS-WeM3 Effect of Nitrogen on Interface Stability of Plasma Enhanced Chemical Vapor Deposition of Hafnium Oxide on Si(100)**, *P. Chen, H. Bhandari, T.M. Klein*, The University of Alabama

Hafnium oxide is a potential high dielectric constant material for use in field effect transistor gate applications. Interface quality, especially for chemical vapor deposited films, is a concern, however, and is the motivation for the introduction of nitrogen. Plasma enhanced chemical vapor deposition (PECVD) was used to grow hafnium oxide thin films on Si using Hf tert-butoxide and $N@sub 2@O$ or $N@sub 2@$ remote plasma. Up to 6 at.% N was obtained using a $N@sub 2@/He$ plasma. Angle resolved x-ray photoelectron spectroscopy indicates the nitrogen is located at the oxide/Si interface. Stability of the interface is enhanced with nitrogen treatment showing a smaller increase in film thickness after annealing in argon.

9:20am **AS-WeM4 High-k Al@sub 2@O@sub 3@-HfO@sub 2@ Layers for CMOS Applications Studied by XPS and ToF-SIMS**, *R.G. Vitchev, L. Houssiau, J.J. Pireaux*, Facultes Universitaires Notre-Dame de la Paix, Belgium

High-k metallic oxides are considered as promising candidates to replace $SiO@sub 2@$ as a gate dielectric in the future CMOS devices. $Al@sub 2@O@sub 3@-HfO@sub 2@$ mixed oxide layers deposited by Atomic Layer Chemical Vapor Deposition on differently pretreated silicon wafers (0.5 nm and 1 nm $SiO@sub 2@$ grown by rapid thermal oxidation as well as HF-last Si surface) were characterized by single- and two emission angle XPS and by ToF-SIMS dual beam depth profiling (250 eV $Xe@super +@$ and $Cs@super +@$ sputtering beam, 15 keV $Ga@super +@$ analysis beam). The composition and the depth distribution of constituent elements were measured for mixed oxide layers deposited with different number of cycles (and hence with different thickness) and different Hf/Al cycle ratios. It was found that the Hf/Al content ratio for the thinnest films was much higher than for the thicker films with the same cycle ratio. The surface region of the thicker films was enriched in Al (and depleted in Hf) indicating a preferential deposition of $HfO@sub 2@$ at the film/silicon interface. The depth distribution of impurities was also measured and compared. The interfacial $SiO@sub 2@$ layer thickness was determined as well as the oxidation state of Si atoms in it. Changes of the interfacial $SiO@sub 2@$ layer thickness and chemistry after prolonged air exposure were followed. Work performed under EU-CUHKO project.

9:40am **AS-WeM5 Materials Characterization and Processing Effects on Hafnium-based Gate Dielectrics**, *W.R. Nieveen*, Charles Evans & Associates/Evans Analytical Group; *P.S. Lysaght*, International SEMATECH; *G. Goodman, I. Mowat, B. Schueler*, Charles Evans & Associates/Evans Analytical Group; *J.A. Bennett, B. Foran, M. Gardner, R.W. Murto, H.R. Huff*, International SEMATECH

Introduction of high-k gate dielectrics into semiconductor processing is proving to be a formidable challenge due to the electrical performance requirements and insufficient understanding of the variations in physical characteristics as a function of thermal processing. Relevant device parameters including gate leakage current density, EOT, $V@sub t@$ instabilities, $V@sub fb@$ shift, and electron and hole mobility are affected by process conditions that alter the materials properties. Such physical parameters include phase orientation, oxygen coordination, onset temperature of crystallization, etc. Optimization of process parameters, which affect the material properties and lead to improved device performance with good integration properties, is today's challenge in high-k materials. In this work, we focus on advanced material characterization of various hafnium-silicon-oxygen composition systems and correlate the physical data with specific aspects of transistor performance. A comprehensive and complimentary set of Hf silicate samples, exposed to an incremental range of thermal process treatments, are characterized by XPS, HRTEM, HAADF, EELS, conductive AFM, and SIMS. Fundamental issues associated with phase separation in Hf-Si-O (and HfSiON) systems are discussed within the context of relevant capacitor and transistor device performance. We will discuss the correlation of physical material parameters measured by various analytical techniques with process conditions, and electrical parameters and measurements.

10:00am **AS-WeM6 Synchrotron UPS and EXAFS Analysis of High-k and Si Interfaces**, *Y.-S. Lin, R. Puthenkovilakam, J.P. Chang*, University of California, Los Angeles

Ultra-thin dielectric films with high permittivity such as $ZrO@sub 2@$, $HfO@sub 2@$, and $HfO@sub x@N@sub y@$ have numerous applications in advanced microelectronics, especially on silicon substrates for gate dielectric application in metal-oxide-semiconductor (MOS) devices. In this work, we combine synchrotron based ultra-violet electron spectroscopy (UPS) and extended x-ray absorption fine structures (EXAFS) analysis to characterize the interface of $ZrO@sub 2@$, $HfO@sub 2@$, and $HfO@sub x@N@sub y@$ on silicon. Specifically, the interfacial composition and chemical coordination of the deposited metal oxides and oxynitrides films on silicon are determined. By tuning the photon energy in UPS analysis, we determined the composition of the interfaces between high-k dielectrics and silicon and their corresponding valence band structures. The experimental results were compared to first principle calculations using density functional theory to validate the measurements and elucidate the effect of chemical coordination at the interface on the electronic structure, band gap, and band offsets. The energy shifts measured in oxygen s and p states compared favorably with first principle calculations and closely related to the bonding to metal atoms. The Fourier transformed EXAFS spectra also agreed very well with the first principle prediction and allowed the determination of interatomic spacings and the chemical nature of the nearest and second-nearest neighboring atoms. Based on the experimental validation, we used density functional theory to calculate the electronic band gaps, conduction and valence band offsets, and interface states for dielectric/Si interfaces, and found that these properties are greatly affected by the metal, oxygen, and nitrogen coordinations.

10:20am **AS-WeM7 Determination of ToF Medium Energy Backscattering Capabilities for Interfacial Analysis**, *R.D. Geil, B.R. Rogers, D.W. Crunkleton, Z. Song, R.A. Weller*, Vanderbilt University

Time-of-flight medium energy backscattering (ToF-MEBS) is a unique surface analysis technique developed at Vanderbilt initially for determining levels of transition metal contaminants on silicon surfaces. The technique's high sensitivity and depth resolution makes it highly suitable for the analysis of ultra-thin films, such as gate dielectrics. The interface between the gate dielectric and silicon is of particular interest because it is a dominant factor in determining the overall electrical properties of the gate structure.¹ In order to determine the extent of information about the lower interface region of a gate dielectric that ToF-MEBS can provide, we have studied a well-characterized material system, $SiO@sub 2@/Si$. Thermally grown $SiO@sub 2@$ films with thicknesses ranging from 2-10 nm were analyzed to determine how interfacial information degrades with depth into the sample. Thickness and stoichiometric information at the bulk and interfacial regions were determined. Channeling in the

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direction of the Si substrate was performed to suppress background. TEM analysis was performed on the films to confirm ToF-MEBS thickness values. Spectroscopic ellipsometry was also used for thickness comparisons. XPS analysis provided extra interfacial and compositional information. @FootnoteText@ @footnote 1@ Wilk, G.D., R.M. Wallace, and J.M. Anthony, High-K Gate Dielectrics: Current Status and Materials Properties Considerations. Applied Physics Review, 2001. 89(10): p. 5243-5275.

10:40am **AS-WeM8 Investigation of PECVD TiO₂ on Silicon, P.R. McCurdy, L. Sturgess, S. Kohli, E.R. Fisher, Colorado State University**
Continuous wave (CW) and equivalently powered, pulsed radio frequency plasmas were used to deposit thin films of titanium dioxide on to Si(100) substrates. In these experiments oxygen plasmas were created by feeding oxygen gas through the coil region, titanium (IV) isopropoxide was introduced downstream from the plasma region. These films have been characterized using XRD, XPS, SEM and AES. XRD showed that TiO₂ films deposited at substrate temperatures $\hat{A}^3350\hat{A}^{\circ}\text{C}$ are polycrystalline with an anatase structure, while at lower substrate temperatures the films were amorphous. Results show high quality films were produced with some carbon incorporation. Annealing these films in vacuum at 900 oC show the TiO₂/Si interfacial region to be reduced to Ti₂O₃, while Si is oxidized to SiO_x. Upon annealing at a 950oC further reduction of the TiO₂ film was noted to include TiO. The 950oC film partially re-oxidized upon exposure to atmosphere. XRD of annealed films showed no crystalline structure of these annealed films. SEM of the TiO₂ film surfaces showed the as deposited films were smooth and structureless and remained so even when annealed at 850oC. Annealing at 950oC caused the surface to become very rough, resulting in the rupturing of the TiO₂ surface thus exposing areas of the underlying Si/SiO₂ substrate.

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Applied Surface Science

Room Hall A-C - Session AS-WeP

Poster Session

AS-WeP1 A Simple Method Identifying the Influence of Photoperturbation Effect on Ultrashallow Junction Images Observed by Scanning Capacitance Microscope, M.-N. Chang, National Nano Device Laboratories, Taiwan, R.O.C.; *W.-W. Wan, J.-H. Lai,* National Tsing Hua University, Taiwan, R.O.C.; *C.-Y. Chen, F.-M. Pan,* National Nano Device Laboratories, Taiwan, R.O.C.; *J.-H. Liang,* National Tsing Hua University, Taiwan, R.O.C.

Scanning capacitance microscopy (SCM) with high sensitivity and high spatial resolution has attracted much interest in profiling two-dimensional carrier distribution and investigating ultrashallow junctions. Atomic force microscope (AFM), equipped with a SCM system, is a typical setup that synchronously provides SCM images and the corresponding topographic images for cross-sectional characterization. In this work, we have provided a simple method to investigate the influence of photoperturbation effect induced by AFM laser beam on ultrashallow junction images observed by SCM. The samples were ultrashallow p⁺ junctions formed by BF₂ implantation at low energies. RTA processes were performed at 1050 °C for different anneal times from 5 to 30 seconds in N₂ ambient. The width and pitch of the designed grating pattern are 0.8 and 2 μm, respectively. It is revealed that the photoperturbation effect induced by AFM laser beam leads to SCM image broadening and junction region narrowing. In other words, the photoperturbation effect not only significantly affects the dC/dV signals but also deteriorates the accuracy of junction characterization, in particular for ultrashallow junctions. The experimental results will be shown and discussed. The section analysis also reveals that there are distorted differential capacitance (dC/dV) profiles in the photoperturbed SCM images. Comparing dC/dV profiles of various photoperturbed SCM images, one can identify the area not affected by AFM laser beam. This simple method allows us to identify the influence of the photoperturbation effect on the pattern region. According to this study, the pattern edge region is more sensitive to the photoperturbation effect than the pattern central region.

AS-WeP2 Wettability Control of Polymer Surface through 126 nm Vacuum Ultraviolet Light Irradiation, Y. Nakanishi, Waseda University, Japan; *A. Hozumi, N. Shirahata,* National Institute of Advanced Industrial Science and Technology, Japan; *S. Asakura, A. Fuwa,* Waseda University, Japan

The surface modification of polymeric materials through vacuum ultraviolet (VUV) light irradiation has attracted much attention due to its wide variety of applications, including improvement of the wettability, biocompatibility and coating adhesion of such surfaces. In this study, we report on the surface modification of poly (methyl methacrylate) (PMMA) using VUV light of 126 nm radiated from an Ar₂* excimer lamp. We have particularly focused on the effects of atmospheric pressure during VUV-irradiation on the surface wettability, chemical structure and morphology of the PMMA surfaces, since atmospheric oxygen plays a crucial role in the photocleavage of polymeric chains and subsequent photooxidation. Each of the samples was exposed to VUV light for 1~50 min under various pressures of 3x10⁻⁴, 10, 10³ or 10⁵ Pa. Hydrophobic PMMA surface became hydrophilic during VUV irradiation conducted over the pressure range of 10⁻⁴~10⁵ Pa. However, the degree of hydrophilicity of the modified surface was primarily determined by the atmospheric pressure. The minimum water-contact angles of the samples treated at 10, 10³ and 10⁵ Pa were about 49, 31 and 64°, respectively. On the contrary, in the case of 3x10⁻⁴ Pa, PMMA surface became highly hydrophobic with its contact angle changing from 80 to about 100°. As confirmed by X-ray photoelectron spectroscopy, at 3x10⁻⁴ Pa the C concentration and the intensity of the C-C groups in the C1s spectra increased. This was probably due to crosslinking reactions including the formation of new C-C bonds. Since the oxidation reactions did not proceed efficiently under such high vacuum condition, the free radicals may have recombined and crosslinked with each other, resulting in the increase of C-C groups. These results indicate that surface wettability of the PMMA substrates might be controllable by selecting the atmospheric pressure during 126 nm VUV irradiation.

AS-WeP3 An XPS Comparison of ALD and PLD Grown Thin Al₂O₃ Layers, A.I. Zinine, J.M. Sturm, R.G. Bankras, H. Wormeester, B. Poelsema, University of Twente, The Netherlands

Atomic Layer Deposition (ALD) is regarded as a suitable deposition technique for high-K metal oxides. Pulsed Laser Deposition (PLD) is an attractive alternative for a fast identification of new materials. A comparative XPS study of thin Al₂O₃ films grown by ALD (5, 10 and 20 nm) and PLD (15 and 30 nm) was made. This analysis is possible without a sputterprofile and is thus not compromised by co-sputtering. Water and trimethylaluminum were used as precursors in the ALD process. Fully oxidized alumina films with good stoichiometry and a band gap of 6.8±0.1 eV were obtained in all cases. The Si 2p XPS peak of the ALD films grown on hydrogen terminated Si with 50 ALD cycles did not show the formation of SiO₂. Angle resolved measurements gave a thickness of 4.2 nm, while a film grown on silicon oxide was 5.0 nm thick as expected for 50 cycles for the recipe used. This indicates growth inhibition in the first case. We note that both films showed a negligible carbon contamination. Freshly prepared ALD samples showed an O 1s XPS peak, composed of oxygen bonded to aluminium and a 1.6 eV energy shifted feature. Angle dependent measurements showed that this shifted feature is limited to the two topmost layers and can be identified as an OH species. Prolonged air exposure introduced a third component, which is attributed to oxygen bonded with carbon. The PLD samples grown in oxygen or argon ambient pressures of 0.1 mbar showed both a significant carbon content. However, only samples prepared in oxygen ambient exhibited carbide contamination and oxidized interfacial silicon.

AS-WeP4 Plasma Etching of (Ba,Sr)TiO₃ Thin Films for DRAM Applications, G.H. Kim, C.I. Kim, D.P. Kim, K.T. Kim, Chung-Ang University, Korea

(Ba,Sr)TiO₃ (BST) thin film attracts a great interest as a new dielectric material in capacitors for the next generation ultralarge scale integrated dynamic random access memories, such as giga bit DRAM in the wide range of research institutes to semiconductor industries because of its large dielectric constant, low leakage current, low dielectric loss, lack of fatigue, and low Curie temperature. A lot of papers have been presented on BST film characteristics using growth methods, however, its patterning have been studied less. In order to realize the higher integration, it is important to minimize the dimension of storage capacitors, simplify the memory cell structure and maintain sufficient accumulated electric charge within a smaller capacitor. Although BST thin films are excellent capacitor dielectric materials for DRAMs, several problems such as fine pattern transfer and no plasma induced-damage etc. In order to solve these problems, the etch behavior of BST with Ar/Cl₂/CF₄ gas mixtures is investigated with inductively coupled plasma (ICP). In this study, ICP etching system was used for BST etching. The etching characteristics of BST thin films were investigated in terms of etch rates and selectivity as a function of Cl₂/Ar and additive CF₄ into Cl₂/Ar, rf power, dc bias voltage and chamber pressure. The Cl₂/Ar and additive CF₄ into Cl₂/Ar plasmas were characterized by optical emission spectroscopy and Langmuir probe analysis. The chemical states on the etched surface were investigated with x-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

AS-WeP5 Dielectric Properties of Epitaxial Growth (Pb, Sr)TiO₃ Thin Films on Al₂O₃ (100) Substrate, K.T. Kim, C.I. Kim, Chung-Ang University, Korea

Electrical tunable dielectric devices rely on the variation of a ferroelectric materials dielectric constant with application of an electric field. The requirements of Ferroelectric materials are low dielectric constant, high tunability, low losses and low leakage current. The structure and morphology of the films were characterized using X-ray diffraction and scanning electron microscopy. We investigated on the structural, electrical properties of (Pb_{0.5}Sr_{0.5})TiO₃ thin films on the Al₂O₃ (100) substrate prepared using MOD method. From the XRD analysis, the peak in the XRD pattern of PST thin films on the Al₂O₃ substrate was shown epitaxial growth. The low loss (~0.001) and high tunability (~60%) were obtained for (Pb,Sr)TiO₃ thin films on the LaNiO₃ substrate measured at 1 GHz. This work was supported by Korea Research Foundation Grant (KRF-2001-042-E00042).

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AS-WeP6 Ferroelectric Properties of Bi₂La₂O₇/TiO₂ Thin Films on (111)-oriented LaNiO₃ Electrodes, C.I. Kim, K.T. Kim, Chung-Ang University, Korea

The BLT thin films were prepared by using metal organic decomposition method. The structure and morphology of the films were analyzed by x-ray diffraction (XRD), atomic force microscope (AFM), and Scanning electron micrograph (SEM). SEM and AFM showed uniform surface of the films. The LNO thin films annealed at temperature as high as 600 °C exhibit the (100)-oriented structure. The BLT thin films were found to crystallize preferably with (111)-oriented grains on LNO bottom electrode annealed at 600 °C for 1h. However, the BLT thin films were grown using a Pt bottom electrode showed a polycrystalline phase. The BLT thin films grown on LNO thin films showed excellent ferroelectricity and higher remanent polarization than BLT thin film using a Pt electrode. The remanent polarization P_r and coercive field is 22.5 mC/cm² and 120 kV/cm. The BLT thin films on LNO bottom electrode exhibited no significant degradation of switching charge at least up to 5x10⁹ switching cycles at a frequency of 50 kHz below cycling fields of 5 V. It was shown experimentally that there was no data loss after 3x10⁴ s of memory retention at room temperature.

AS-WeP7 Distinguishing the Dependence of the Apparent Local Barrier Height on Measurement Conditions, S. Yagyu, M. Yoshitake, National Institute for Materials Science, Japan; Y. Mizuno, R.E. Kirby, Stanford Linear Accelerator Center

Work function is an important and fundamental property of materials related to the electron emission and reaction of molecules on the surface. As functional materials of reduced dimension become increase, the measurement of the local work function becomes important. The apparent local barrier height (LBH) related to the local work function has been measured by STM. The LBH is not the local work function of a sample material but multi-parameters value correctly, because the LBH based on the STM technique depends on the tip parameters (material, shape), the measurement parameters (tunnel current (I), bias voltage (V) and tip-sample separation (s)) and certainly the local work function of the sample material. Since each LBH obtained on same material surface with various measurement parameters is extremely different, we should know relation between the measurement parameters and the LBH. In STM/LBH measurement a I is proportional to a V and a s. For example, if we fix a I and change a V, a s is changed automatically. We measured dependence of the LBH on the I, V, and s precisely on the reconstructed Au (111) surface with an Au tip. The results under three different conditions, a constant s, I, and V were compared in the low bias voltage range (-50mV to -5mV) where I-V curve shows linear (ohmic). Under a constant s, the LBH does not change with the V, indicating that the LBH is independent of the V. Under a constant I, the LBH increases with the increased V. Under a constant V, the LBH increases with the increased s. The three results indicate that LBH depends exclusively on the s in our experimental conditions.

AS-WeP8 The Systematic Study of Ga TOF SIMS High Mass Molecular Ion Registration, Composition and Fragmentation of Selected Peptide Hormones on Silver Substrate, H Chen, College of William and Mary and Incogen, Inc.; A. Wilkerson, College of William and Mary; D. Malyarenko, College of William and Mary and Incogen, Inc.; E. Tracy, Applied Research Center and College of William and Mary; D. Manos, Applied Research Center and College of William and Mary.

This paper reports the use of Ga⁺ SIMS to provide imaging simultaneously with high sensitivity and specificity for peptide hormone registration. Although this technique is developed for high molecular weight organic polymers on silver and gold, no similar systematic quantitative studies are reported for biopolymers. We report high resolution spectra obtained by ToF-SIMS for molecular ions of Vasopressin II, Human Angiotensin and Somatostatin adsorbed on silver substrate. Characteristic positive high-mass parent peaks and adducts have been identified. The mass resolution exceeds 2000 for all three peptides. The dependence of the yield for the parent peak on solution concentration has been studied for Angiotensin. Parent peak intensities comprise from 1 to 15 % of the intensity for identifiable fragments. Images confirm that the fragmentation is associated with multi-layer formation. Parent peak adducts reproducibly display the anticipated quantitative isotope ratios and are skewed toward high masses. Sodium contamination adducts are registered as well. The images of surface coverage are reported at the parent masses. Unlike MALDI, no multiply charged species, ladder fragmentation or dimers are observed in the intermediate mass range. The low molecular weight peaks (below 200 Da) have characteristic signatures of the amino acid content for the peptides.

AS-WeP9 Analysis of Silane Coupling Compound Monomolecular layer on Sapphire Glass used by TRXPS, T. Tazawa, JEOL Ltd., Japan; C. Mochizuki, M. Shibata, University of Yamanashi, Japan; Y. Iijima, JEOL Ltd., Japan

Recently, the material which spreads silane coupling compound is actively researched. This material is usually applied to the fabrication of chip level interconnects, ohmic contacts, and printed circuit boards, and plating. Moreover, the application to life sciences is expected as for this compound. However, the thickness of silane coupling compound is very thin. In general, silane coupling compound is used by one or two molecular layers. Therefore, the analysis of interface between silane coupling compound and the base material surface becomes important. The interface and surface for this material is useful analyzed with XPS, because silane coupling compounds are organic compounds. It is difficult to measure interface information accurately in a normal XPS analysis, because the thickness of silane coupling compound is thin. There is total x-ray reflection photoelectron spectroscopy (TRXPS) as a method of solving this problem. The use of x-ray total reflection has become noteworthy in photoelectron spectroscopy. The angular dependence of photoelectron peak intensities corresponds to the position change in the standing wave was caused by change in the x-ray glancing angle. Especially, at the measurement of multi-layer film and/or monomolecular layer formed on glass or Si wafer, because the belly and the paragraph position of standing wave of x-ray can be adjusted in such a way that they coincide with the respective layer position by changing the glancing angle. In this work, we examined silane coupling compounds monomolecular formed on sapphire glass measured by TRXPS. The profile of photoelectron intensity was observed to grazing incidence x-ray with C and Si. As the result, it is observed that the island structure of silane coupling compounds formed on the glass surface.

AS-WeP10 Electronic Structure of Carbon Nanotube Filled with Cs, Y.J. Song, H. Kim, Seoul National University, Korea; G.-H Jeong, R. Hatakeyama, Tohoku University, Japan; Y. Kuk, Seoul National University, Korea

As one of the most promising candidate materials for nanoelectronic devices, a carbon nanotube (CNT) has attracted much interest for its ideal electrical properties. The properties of a pristine CNTs are now well understood after studies with scanning probe microscope, transmission electron microscope, raman spectroscopy and transport measurements. CNTs can be semiconducting or metallic, but their electronic properties cannot be controlled since they are determined by uncontrollable chirality. Recently it has been suggested that the local modification of their electronic properties can be done by inserting or adsorbing various molecules into or on the side wall of CNTs. The modification of the local density of states can be utilized to produce nanometer-scale electronic devices. Filling metals into CNTs produce local metallic nanotubes. We have chosen to fill CNTs with Cs. We studied the geometric and electronic structures of these CNTs. The local change in the geometric structure implies the modification of CNT with Cs metal filling. That was confirmed by measuring the shift of the van Hove Singularities in scanning tunneling spectroscopy. Partially filled Cs metal chains in CNT seems to work as carrier dopants.

AS-WeP11 Investigation of Secondary Cluster Ion Emission from Self-Assembled Monolayers of Alkanethiols on Gold with TOF-SIMS, S. Sohn, M. Schröder, H.F. Arlinghaus, Westfälische Wilhelms-Universität, Germany

Self-assembled monolayers (SAMs) of alkanethiols on gold are ideal model systems for studying the emission processes of secondary ions from thin organic layers on metal substrates under keV ion bombardment. In this experimental study, we focus on the emission processes of gold-alkanethiolate cluster ions, which are not well understood yet. For this purpose we carried out time-of-flight secondary ion mass spectrometry (TOF-SIMS) measurements on SAMs of different alkanethiols CH₃(CH₂)_nSH with various alkyl chain lengths (1 ≤ n ≤ 17) on gold substrates. The gold-alkanethiolate cluster ions Au_xM_y with M = CH₃(CH₂)_nSH, 1 ≤ x ≤ 7 and x-3 ≤ y ≤ x+1 show intense peaks in negative mass spectra of all investigated alkanethiol SAMs under 10 keV Ar⁺ bombardment. Around the corresponding peaks, a characteristic peak pattern of additional ions is observed. We analysed the contribution of different cluster ions formed by an attachment or a loss of up to five hydrogen atoms and their isotopy to the individual peaks of the peak pattern. We found two different types of gold-alkanethiolate cluster ions. The first type has only one parent ion, which has no hydrogen atom attached. The second type has two parent ions, one with no attachment of additional hydrogen atoms and another with one additional hydrogen atom. Moreover, we found a universally valid sum formula, which predicts

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the most intense peak in the peak pattern of gold-alkanethiolate cluster ions of all investigated alkanethiol SAMs.

AS-WeP12 Multivariate Statistical Analysis of Time of Flight Secondary Ion Mass Spectrometry Images, Looking beyond the Obvious, V.S. Smentkowski, General Electric Global Research Center; *J.A. Ohlhausen, M.R. Keenan, P.G. Kotula,* Sandia National Laboratories

Analytical instrumentation such as Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provides a tremendous quantity of data since an entire mass spectrum is saved at each pixel in an ion image. The analyst often selects only a few species for detailed analysis; the majority of the data are not utilized. Researchers at Sandia National Laboratory (SNL) have developed a powerful Multivariate Statistical Analysis (MVSA) tool kit named AXSIA (Automated eXpert Spectrum Image Analysis) that looks for trends in complete data sets (eg. analyzes the entire mass spectrum at each pixel). A unique feature of the AXSIA tool kit is the generation of intuitive results (eg. negative peaks are not allowed in the spectral response). The robust statistical process is able to unambiguously identify all of the spectral features uniquely associated with each distinct component throughout the data set. GE and Sandia used AXSIA to analyze raw data files generated on an Ion ToF IV ToF-SIMS instrument. Select examples will be shown. The MVSA toolkit positively identified metallic contaminants within a defect in a polymer sample. These metallic contaminants were not identifiable using standard data analysis protocol. We will also demonstrate that the MVSA toolkit is able to analyze images collected using the burst pulsing mode. This work was funded in part under CRADA SC00/01609 PTS 1609.02 Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

AS-WeP13 Surface Composition of Polyurethane Foams with Accelerated Aging, J. Manzerova, D. Parsons, University of Nevada, Las Vegas; *S.W. Yu,* Lawrence Berkeley National Laboratory; *D.W. Lindle, A.L. Johnson,* University of Nevada, Las Vegas

Polyurethane foams find broad application as structural and insulating (shock, electrical, etc.) materials. The long term stability of these materials are of particular interest. We have studied ReCrete and TDI types of polyurethane foams by means of the near edge x-ray absorption fine structure (NEXAFS) spectroscopy and the x-ray photoelectron spectroscopy (XPS). The foams were subjected to accelerated aging studies (60C and 80C under atmospheric conditions) for times up to 2 years. Systematic shifts in composition of the surface of the samples were found. Spectral assignments will be given and issues having to do with the variability of the surface of the polyurethane with temperature and environmental exposure will be addressed.

AS-WeP14 Field Emission Electron Spectroscopy of Clean and Oxidized Mo Single Tips, X. Zhao, R.A. Outlaw, R.L. Champion, D. Manos, B.C. Holloway, The College of William and Mary

We have constructed a multi-functional apparatus to characterize surfaces by ARAES, ARXPS, EELS and TDS both prior to and after, measurement of field emission spectra. The fine structure of field emission energy distributions, in concert with these adjunct surface analyses, provides information of both bulk band structure and localized electronic structure as a function of adsorbate uptake. This paper reports measurements of field emission spectra taken on a 10 nm radius Mo tip under UHV ($\sim 10^{-10}$ torr), and as a function of exposure to controlled doses of CO and O₂. Effective work functions are extracted from Fowler-Nordheim plots and show variation over the range of gas dosage. Field emission theory with total energy representation (TED) is used to further interpret the spectra and to elucidate the effects of oxygen bearing adsorbates.

AS-WeP15 Optical, Structural and Electrical Characteristics of High Dielectric Constant Zirconium Oxide Thin Films Deposited by Spray Pyrolysis, M.A. Aguilar, CICATA-IPN, Mexico, Spain; *G. Reyna,* UAM-I, Mexico; *M. Garcia, J. Guzman,* IIM-UNAM, Mexico; *C. Falcony,* CINVESTAV-IPN, Mexico

High dielectric constant zirconium oxide thin films have been deposited on silicon substrates at temperatures from 400 to 600°C, using the spray pyrolysis technique. The films were deposited from two spraying solutions (0.033 and 0.066M) of zirconium acetylacetonate dissolved in N,N-Dimethylformamide. The as deposited films were stoichiometric, transparent and with a very low surface roughness (5-40Å). The films present a dielectric constant in the range from 12.5 to 17.5, depending on

the experimental conditions. The films deposited at 500°C and with the 0.066M spraying solution can stand electric fields up to 3 MV/cm, without observing destructive dielectric breakdown. X ray diffraction as well as transmission electron microscopy measurements indicate that the films are polycrystalline. Infrared spectroscopy show the existence of silicon dioxide (SiO₂) in the films. Spectroscopic ellipsometry indicates that SiO₂ as well as ZrO₂ and c-Si conform a roughness layer located at the ZrO₂/Si interface. The presence of this interface layer, as well as the overall optical and structural characteristics of the films prepared, are probably responsible for the good dielectric characteristics observed on them.

AS-WeP16 Using MEMS Microarrays and Neural Networks to Identify Preferred Surface Chemistry in Application-Specific Gas Sensing, Z. Boger, R.E. Cavicchi, D.C. Meier, C.B. Montgomery, S. Semancik, National Institute of Standards and Technology

Surface chemical interactions between target analytes and sensing films are of primary importance in determining gas sensor performance. However, selecting the most appropriate sensing materials and conditions to detect certain analytes in different gas monitoring applications is very difficult. We present a novel approach for identifying well-suited thin film and surface compositions, preferred microstructures, and operating temperatures for conductometric gas sensing. It employs response databases measured from multi-element MEMS microarrays as well as artificial neural networks (ANN) signal processing. The array elements are microsensor platforms that contain varied sensing film types (TiO₂ and pure and surface-modified SnO₂), and can be programmed to operate individually at a variety of temperatures (20 °C to 500 °C), while the composition of test gases is changed. Recursive ANN pruning and re-training techniques are used to identify the more relevant inputs (materials, temperatures) for recognizing and quantifying a specific analyte in a given background. We describe several example cases involving pure and metal-dosed oxide films for: 1) recognition of 6 gases (H₂, ethanol and varied VOCs); 2) estimation of concentrations for binary mixtures of H₂, methanol and acetone in the 5-200 ppm (micromole/mole) range; 3) concentration estimation of chemical warfare agents (sarin, tabun, sulfur mustard) and simulants in the range of several ppb (nanomole/mole) to several ppm. Greatly reduced subsets of materials and temperatures, in the range of 3-15 out of a possible 80-1260 combinations, have been shown to carry the most effective analytical information. These selected interfaces and operating conditions provide a basis from which to understand, and then predict, the adsorption, desorption and reaction behavior that are critical to solid state transduction processes for varied classes of gaseous compounds.

AS-WeP17 Nitrogen Doped Carbon Nanoflake Field Emitter Synthesized by RFI PECVD on Patterned Nickel Catalyst Layer, M. Zhu, J. Wang, R.A. Outlaw, X. Zhao, N.D. Theodore, College of William and Mary; *V.P. Mammana,* International Technology Center; *B.C. Holloway, D. Manos,* College of William and Mary

This paper reports the synthesis of a novel morphological form of carbon, which we call carbon nanoflake (CNF), using high-density RF inductively coupled plasma enhanced chemical vapor deposition. We observe that CNF grows rapidly in contact with a Ni catalyst which has been created using a self-assembling nano-sphere lithographic method. Experiments were performed using mixtures of hydrocarbon feedstock (methane or acetylene) diluted in hydrogen to deposit CNF onto the Ni catalyst pattern lying either on a doped-Si wafer, or lying on 300 nm of SiO₂. The gas composition was varied systematically from 10% to 100 % hydrocarbon. Pressure and temperature were varied over a small range in the vicinity of $p = 10^{-1}$ Torr and $T = 680^\circ\text{C}$. We have also performed CNF deposition under conditions to produce nitrogen-doped CNF. SEM images show that the carbon nanoflake has edges less than 10nm wide and that the surface morphology changes with gas composition. CNF structures appear to be robust and well-suited for potential applications in field-emission devices. Kelvin Probe measurements show that the contact potential (work function) of CNF is close to that of graphite. Raman spectra show that the ratio of D to G peaks is a function of the gas composition. The paper also reports field emission tunneling parameters extracted from Fowler-Nordheim I-V curves and field emission spectra (FES).

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AS-WeP18 Microsensor Technique for Analyte Surface Coverage vs. Sensor Response Correlation, A.G. Shirke, R.H. Jackson, B.G. Frederick, The University of Maine; *R.E. Cavicchi, S. Semancik,* National Institute of Standards and Technology; *M.C. Wheeler,* The University of Maine

This paper presents results based on the combined use of a single microsensor platform (as a Temperature Programmed Desorption [TPD] device) with a sensitive, calibrated mass spectrometer that has a minimum detection limit of 10^{10} molecules/s. Desorption kinetics of model systems have been investigated as part of an effort to develop a technique for correlating the relative surface coverages of gas analytes to the electrical responses of chemical sensors. The pulsed-TPD technique takes advantage of the rapid heating characteristics of micromachined sensor platforms (called microhotplates) which are layered structures developed at NIST. Microhotplate sensors include a sensing film, electrodes, and a polysilicon heater all separated by insulator layers. Previous microheater desorption experiments utilized arrays with large numbers of devices to provide enough desorption flux for detection while maintaining the rapid heating rate (over 10^6 K/sec) of the individual devices. Unlike the current experiments that use single microsensors, the large array studies did not explore conductance changes of sensing films. The model system described in this work, condensed benzoic acid on the microsensor surface, is used to evaluate the challenges involved in extension of the technique to actual sensor systems. The experiments were conducted at a base pressure of 5×10^{-10} Torr, using a constant, directed-dosing arrangement for benzoic acid (vapor pressure: 7×10^{-3} Torr at 300 K). A voltage pulse of 500 ms duration was used to heat the polysilicon heater to temperatures up to 700 K within approximately 3 ms while the isothermal desorption flux was monitored by the differentially-pumped mass spectrometer. Limitations and modifications in the data acquisition, sample mounting, and minimum detectable desorption flux are discussed along with the presentation of the desorption isotherms.

AS-WeP19 High Spatial Resolution XPS Analysis of Si Samples Prepared using the FIB Lift-out Technique, J. Fenton, J.E. Fulghum, University of New Mexico; *L.A. Giannuzzi,* FEI Company; *F.A. Stevie,* North Carolina State University

The FIB lift-out technique is increasingly utilized to prepare a wide variety of samples for SEM and TEM analysis, although there have been few studies of sample preparation-related changes in surface chemistry. The goal of this project is to assess the impact of Ga contamination resulting from FIB lift-out preparation of Si. X-ray photoelectron spectroscopy (XPS) has become an increasingly useful characterization technique for such samples due to recent advances in imaging and small area analysis. The Ga distribution on the Si surface, and the impact of sample preparation on surface oxidation, were evaluated using high spatial resolution XPS. The SiO₂ thickness and uniformity were compared with Si from a control sample, which was not exposed to the FIB Ga source. Both quantitative, high spatial resolution imaging and spectra-from-images methods were used to characterize Ga and SiO₂ distributions. These methods are required for accurate characterization of the FIB samples, as the samples are generally smaller than the areas analyzed using small area spectroscopy methods.

AS-WeP20 Ion Beam Alignment of Liquid Crystals on Polymer Substrates, S. Pylypenko, K. Artyushkova, J.E. Fulghum, University of New Mexico; *L. Su, L. West,* Kent State University; *Y. Reznikov,* Ukraine Academy of Science

Liquid crystal alignment is generally obtained through rubbing methods that require direct contact with the alignment surface. Non-contact methods could solve many of the problems that result from rubbing. One of the latest non-contact techniques for alignment of liquid crystals, ion beam alignment, has become a promising substitute for the conventional method based on mechanical rubbing. Although LCD prototypes have been fabricated using the ion beam alignment technique, there is incomplete understanding of both the macroscopic and microscopic alignment mechanisms. Organic and inorganic alignment layers were studied using X-ray Photoelectron Spectroscopy (XPS) and Polarized Attenuated Total Reflection Infrared Spectroscopy (ATR-IR) to characterize chemical changes and surface anisotropy to the alignment substrate. The surface analytical characterization results have been correlated with measurements of liquid crystal alignment and pre-tilt angle measurement to enhance our understanding of non-contact alignment.

AS-WeP21 Relation between RF Breakdown and Particles Contamination on RF-Processed X-band Structures, F. Le Pimpec, S. Harvey, R.E. Kirby, F. Marcelja, SLAC

X-band accelerator structures meeting the Next Linear Collider(NLC) design requirements have been found to suffer damage due to Radio Frequency (RF) breakdown when processed to high gradients. Improved understanding of these breakdown events is desirable for the development of structure designs, fabrication procedures, and processing techniques that minimize structure damage. RF reflected wave analysis and acoustic sensor pickup have provided breakdowns localization in RF structures. Particles contaminant, after the clean autopsy of 3 RF-processed travelling wave structures, have been catalogued and analyzed. Their influence on RF breakdown will be discussed.

Wednesday Afternoon, November 5, 2003

Applied Surface Science

Room 324/325 - Session AS-WeA

Fuel Cell & Battery Materials/Corrosion

Moderator: B. Beard, Akzo Nobel Chemicals Inc

2:00pm **AS-WeA1 Development of Multi Layered Oxide Nanofilms for Fast Oxygen Ionic Conduction**, *S. Thevuthasan, S. Azad, O.A. Marina, C.M. Wang, V. Shutthanandan, L.V. Saraf, D.E. McCready, I. Lyubinetzky, A. El-Azab, C.H.F. Peden*, Pacific Northwest National Laboratory

There has been considerable interest in solid oxide fuel cell (SOFC) devices since they provide relatively clean alternative energy to the conventional fossil fuels. Several research groups are working on developing electrolyte materials with higher oxygen ionic conductivity at low temperatures to improve the efficiency of SOFC device at low temperatures. It is well known that nanoscale materials often display properties very different from the base coarse-grained bulk materials. In particular, it has been recently demonstrated that a nanoscale lamellar structure of two different fluorides (calcium fluoride and barium fluoride) can exhibit significantly higher ionic conductivity along the interfacial directions at moderate temperatures. If such a remarkable finding could be transferred into practice, it would provide the ability to design similar structures from oxygen ion conductors to enhance the performance of SOFC devices at temperatures substantially lower than the current operating temperatures. In this study, we investigated the effect of multiple interfaces on oxygen ionic conductivity in Gd-doped single crystal ceria/zirconia multi layers as a function of Gd concentration. Pure and Gd-doped ceria and zirconia films were grown by oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and characterized by reflection high-energy electron diffraction (RHEED), x-ray diffraction (XRD), Rutherford backscattering spectrometry (RBS) and high-resolution transmission electron microscopy (HRTEM). The preliminary results are encouraging and four layered Gd-doped ceria/zirconia multi layered structure shows higher oxygen ionic conductivity compared to two layered structures. @FootnoteText@ @footnote 1@N. Sata, K. Eberman, K. Eberl and J. Maier, Nature 408 (2000) 946.

2:20pm **AS-WeA2 Surface Science Studies of Model Fuel Cell Electrocatalysts**, *P.N. Ross*, Lawrence Berkeley National Laboratory **INVITED**

Progress in the understanding of the electrocatalytic reactions in fuel cells will be reviewed. The emphasis is on the study of model electrocatalysts with in-situ surface spectroscopies. It is shown that Pt single crystals and well-characterized Pt bimetallic bulk alloys have been used with some success as models for real (commercial) catalysts. The electrode reactions discussed include hydrogen oxidation evolution, oxygen reduction, and the electrooxidation of C1 compounds (carbon monoxide, formic acid, and methanol). Surface spectroscopies discussed are infrared reflection absorption spectroscopy (IRRAS), scanning tunneling/atomic force microscopy (STM/AFM), and surface x-ray scattering (SXS). The discussion will focus on the relation between the energetics of adsorption of intermediates and the reaction pathway and kinetics, and how the energetics and kinetics are effected by extrinsic properties of the model system, e.g. surface structure and composition. Finally, we conclude by discussing some limitations of these model systems and suggest some directions for studying more realistic systems with the same rigor.

3:00pm **AS-WeA4 Identifying Factors Responsible for Capacity and Power Loss in Lithium-ion Cells**, *D. Abraham*, Argonne National Laboratory **INVITED**

High-power battery technology is crucial to the commercial success of hybrid electric vehicles. In the United States, high-power lithium-ion batteries are being studied as part of the Advanced Technology Development (ATD) program. Lithium ion-cells, ranging in capacity from 1 mAh to 1Ah, are built and tested to determine suitable electrode-electrolyte combinations that will meet the calendar life, safety and cost goals of the ATD program. The cells are aged, cycled, and/or abused according to established test procedures. After test completion, the cell components are examined by various diagnostic tools to determine the nature and extent of physical, chemical, and structural changes that resulted from the testing conditions. These diagnostic results are used to improve cell chemistries and cell designs of the next generation of lithium-ion batteries. The capacity and power loss of lithium-ion cells are governed by the chemical and electrochemical side reactions that occur at the electrode-electrolyte interface. The formation of a Solid Electrolyte Interface (SEI) layer on negative electrodes that are polarized below electrolyte reduction potential (~0.8 V vs. Li/Li+) is a well-known

phenomenon. The SEI layer, which contains various organic and inorganic electrolyte decomposition products, protects the negative electrode from further reduction and allows stable lithium-intercalation processes at low potential. Capacity loss appears to result from changes and growth of the SEI layer during cell aging. The cell power loss results from impedance increases at the positive electrode, which may be the consequence of changes in the electrode surface films. Data from X-ray photoelectron spectroscopy, secondary ion mass spectroscopy, transmission electron microscopy, electron energy loss spectroscopy, and nuclear magnetic resonance analysis will be presented to support the conclusions of our study.

3:40pm **AS-WeA6 The Chemical Nature of LiCoO₂, LiNiO₂ and LiCo_{0.5}Ni_{0.5}O₂ Surfaces by X-ray Photoelectron Spectroscopy**, *M.A. Langell*, University of Nebraska; *A.W. Moses*, University of California; *J.G. Kim*, University of Nebraska

Many lithium metal oxides find use in lithium batteries as a result of their Li⁺/Li redox properties coupled to their high lithium conductivity and their ability to be multiply cycled between the near-stoichiometric and severely de-lithiated electrode material. In its stoichiometric form, LiCoO₂ presents a straightforward picture in charge balance. Lithium is formally Li⁺, cobalt is Co³⁺ and, with the exception of the occasional defect, the lattice oxygen is comparable to that found in 3d transition metal monoxides, O²⁻. By simple analogy, LiNiO₂ should contain nickel formally in its Ni³⁺ oxidation state. Ni³⁺ is not as thermodynamically favored as the low-spin, octahedrally-coordinated Co³⁺, however, and this tends to destabilize the LiNiO₂ surface composition. We present results from XPS and Auger electron spectroscopy that show LiCoO₂ forms stable, stoichiometric surface compositions once surface hydroxylation and carboxylation are properly taken into account. These latter surface adsorbates are variable, depending upon the history of the material and the surface pretreatment prior to UHV analysis. LiNiO₂, however, is not as well behaved, even when XRD indicates that the bulk is well-ordered. The surface is severely depleted in lithium and phase separation to NiO and cubic LiNiO₂ is common. Adding cobalt to the lattice does not completely stabilize the structure and LiCo_{0.5}Ni_{0.5}O₂ substrates behave much like LiNiO₂ from the viewpoint of the nickel with nickel found predominantly in the Ni²⁺ state. In contrast to literature reports that nickel is Ni²⁺ in LiNiO₂, with charge compensation resulting from a localized Ni²⁺ - O⁻ adjacent lattice ion pairs, we see no evidence that the oxygen is significantly different in the three materials, at least within the near-surface area.

4:00pm **AS-WeA7 Formation of Protective Coatings on Depleted Uranium - 0.75 wt% Titanium Alloy**, *D.F. Roeper, C.R. Clayton, D. Chidambaram, G.P. Halada*, SUNY at Stonybrook

The process of enriching uranium for nuclear power plants results in the formation of a toxic and mildly radioactive waste. Exposure to this byproduct called depleted uranium (DU) may have deleterious health effects. The leaching of uranium into the environment and its prevention have become issues of concern. Protective coatings could prevent leaching of DU as well as prevent localized corrosion. In this study, we explore the formation of silicate-based coatings on DU-0.75 wt% Ti alloy (0.75 wt% Ti, less than 0.2 wt% ²³⁵U and ~0.0008 wt% ²³⁴U, rest being ²³⁸U with some trace impurities); a common DU alloy. These coatings are compared with a molybdate-based coating that has been demonstrated earlier. The optimal concentrations of the inhibitors and activators have been used, as determined from the earlier study. The morphological information has been obtained using optical microscopy and scanning electron microscopy. While open circuit potential measurements and potentiodynamic polarization have been utilized for characterization of the electrochemical behavior, the use of X-ray photoelectron spectroscopy has provided the chemical information regarding the coatings. Our results indicate the primary constituent of the coating to be an oxide complex. We discuss the approach currently undertaken to develop protective complex coatings on the alloy surface. The characteristics of these coatings have been compared with other coatings similarly formed using different inhibitors and accelerators. Acknowledgement: The U.S. Army Research Laboratory under contract DAAD190110799 supported this work. Dr. Derek J. Demaree, PhD., has served as contract officer. S. Jones, I. lowles and A. Smith, Lancet, 357 1532 (2001). C.R. Clayton, D.F. Roeper, D. Chidambaram and G.P. Halada, 203rd Meeting of the Electro Chemical Society, Abstract No. 318, April 30, 2003 Paris, France.

Wednesday Afternoon, November 5, 2003

4:20pm **AS-WeA8 The Mechanism of Protection of Mechanical Damages to Chromate Conversion Coatings Formed on Aluminum Alloys**, *D. Chidambaram, C.R. Clayton, G.P. Halada*, State University of New York at Stony Brook

Inhibitive action of dichromate based solutions have been known for nearly a century. Hexavalent chromium present in these coatings is toxic and a well-known mutagenic agent. Aluminum alloys used widely in the aerospace industry are given a treatment to form chromate conversion coatings (CCCs). The development of alternative coatings requires the precise knowledge of the underlying mechanisms of protection offered by hexavalent chromium, which are unclear. Defects or mechanical damages in CCCs are protected without further treatment by "self-healing" properties. "Self-healing" has been associated with migration of chromates to actively corroding sites. The formation of a protective Al(III)-Cr(VI) complex at damaged sites was first suggested by Abd Rabbo et al. Electrochemical techniques have been used in this study to provide a direct observation of the repassivation of a scratch. XPS analysis of pure aluminum exposed to chromate solution indicates the presence of high amount of hexavalent chromium at higher depth of analysis. This result is in agreement with theories proposing the formation of stable Al(III)-Cr(VI) compounds. Atomic force microscopy (AFM) confirmed the physical presence of these compounds. Synchrotron infrared micro spectroscopy (SIRMS) clearly showed the formation of Al(III)-Cr(VI) complex in these regions. Al(III)-Cr(VI) complex was found to form at active regions and protect the surface irrespective of the nature of the chromate source (adsorbed chromate film or CCCs). A novel study involving scratching of AA2024-T3 prior to the formation of CCC was performed. The surface morphology studied using scanning laser confocal microscopy showed the physical presence of some compounds in the scratches. The increase in the hexavalent chromium content with the number of scratches as observed using XANES explained the mechanism of protection of mechanical damages to the CCCs formed on aluminum alloys.

4:40pm **AS-WeA9 The Role of Hexafluorozirconate in the Formation of Chromate Conversion Coatings on Aluminum Alloys**, *D. Chidambaram, C.R. Clayton, G.P. Halada*, State University of New York at Stony Brook

Alodine 1200S[®] process is widely used to form chromate conversion coatings (CCCs) on aluminum alloys. Potassium hexafluorozirconate (K₂ZrF₆) forms a major component of Alodine. Although the roles played by most of the other components of the treatment bath are known, there is no knowledge about the interaction of hexafluorozirconate with aluminum alloys. Electrochemical and surface analytical techniques have been employed to study the nature of interactions between hexafluorozirconate and constituents of aluminum alloy AA2024-T3. AA2024-T3 is widely used in the aerospace industry. Studies on the interactions between major components found in Alodine[®] with aluminum alloys showed maximum activation to occur in the case of hexafluorozirconate pretreatment. This is contrary to the belief that sodium fluoride, another major component of Alodine[®], acted as an activator. Contact angle measurements have also been performed. Hexafluorozirconate was found to decrease the interfacial tension besides leading to increased surface wetting. The results obtained from electrochemical techniques have also been compared with similar studies conducted using other fluoride components found in Alodine such as sodium fluoride and potassium fluoborate. X-ray photoelectron spectroscopy (XPS) has been used to study the surface chemistry of the alloys after exposure to hexafluorozirconate, thereby giving an insight into the mechanism of activation and surface wetting. The results indicate hexafluorozirconate to play an important role in the formation of chromate conversion coatings on aluminum alloys. This will be useful to the development of coatings based on benign components. Acknowledgements The U. S. Air Force Office of Scientific Research under contract F49620-96-1-0479 supported this work. Lt. Col. Paul Trulove, Ph.D. served as the contract officer.

Thursday Morning, November 6, 2003

Applied Surface Science

Room 324/325 - Session AS-ThM

Electron Spectroscopy

Moderator: B.R. Rogers, Vanderbilt University

8:20am **AS-ThM1 Role of Vacuum Technology and Other Drivers in the Development of Surface Analysis**, *C.J. Powell*, National Institute of Standards and Technology

INVITED

A perspective will be given on the development and use of surface analysis, primarily by AES and XPS, for solving scientific and technological problems. Some of the early approaches for AES and XPS analyses will be described together with major developments (e.g., the availability of demountable flanges and suitable pressure gauges) in instrumental capabilities. Information will be presented on growth and trends in instrumental measurements with reduced uncertainties, knowledge of surface sensitivity, and knowledge and effects of sample morphology. Finally, an overview will be given of analytical resources now available for AES, XPS, and SIMS.

9:00am **AS-ThM3 Valence-band X-ray Photoelectron Spectroscopic Studies of Phosphorus Oxides and Phosphates**, *K.J. Gaskell, M.M. Smith, P.M.A. Sherwood*, Kansas State University

Valence band X-ray photoemission can be used to identify subtle chemical differences in surface chemistry. Phosphorus oxides are known in a number of different crystalline forms, and a very large number of phosphates are known some of which contain one phosphorus atom, and others contain condensed phosphates with a number of phosphorus atoms in chains, rings and three dimensional structures. The phosphorus oxides can be distinguished from the many phosphate species by valence band X-ray photoelectron spectroscopy (XPS), which is also able to distinguish between different crystalline forms of the oxides. The paper will give an overview of the phosphorus/oxygen valence band spectra, with the spectra interpreted by spectra predicted by band structure and cluster calculations. The paper will also describe how oxide free thin (less than 100@Ao@) films of phosphate species can be formed on metal surfaces, with the phosphate composition altered by changing the pH of the solution used to generate the films, and by changing the type of phosphorus acid used. The work provides an example of how valence band XPS can be especially valuable in the characterization of surface films when it is important to identify small chemical differences. This material was based upon work supported by the National Science Foundation under Grant No. CHE-0137502.

9:20am **AS-ThM4 Application of Electron Based Spectroscopies Combined with Chemical Derivatization for the Characterization of Black Carbon Surfaces**, *L.A. Langley, T.H. Nguyen, W.P. Ball, D.H. Fairbrother*, Johns Hopkins University

Black carbon (BC) is derived from charred plant materials and soot from combustion processes and is ubiquitous in the environment. It is now recognized that remarkably small concentrations of BC can have strong effects on the sorption of hydrophobic organic chemicals (HOCs). Despite the ubiquity of such BC particulates and the importance of sorption to contaminant fate and treatment, little is known about the physical and chemical variability of BC materials or the manner in which their properties can impact the sorption of HOCs in aquatic environments. The surfaces of soots and chars are best described as extended graphene sheets decorated at the edges by various surface oxides. The nature and composition of these surface oxides is believed to play a critical role in determining the sorption properties of BCs towards HOCs. Although X-ray Photoelectron Spectroscopy (XPS) can provide information on the elemental composition of the surface and detect changes in the O/C ratio of different BCs, quantification of the distribution of surface oxides by analysis of the C(1s) and O(1s) lineshapes alone is very difficult. To circumvent this problem XPS augmented by chemical derivatization has been employed in order to provide quantitative information on the distribution of oxide functional groups on the surface of BC. We will also present results on the potential application of bromine as a chemical derivatizing agent capable of titrating the degree of aromatic character in BCs. Additionally, synthetic chars generated from the pyrolysis of wood samples will be characterized as a function of their formation conditions. Results from XPS and chemical derivatization studies of natural chars and synthetic chars will be presented. These results are complemented by sorption studies, where different trends in sorption can be rationalized based on the surface characterization of the BC sorbents.

9:40am **AS-ThM5 Comparison of X-ray and Electron Beam Induced Damage Rates**, *A.S. Lea, M.H. Engelhard, D.R. Baer*, Pacific Northwest National Laboratory

While many people are aware of the effects of damaging electrons during Auger electron spectroscopy or electron microscopy, x-ray induced changes in specimens frequently occur and may be more common than often recognized or noted in the literature. Although electrons interact strongly with samples with a high damage cross-section and x-rays of similar energies interact less strongly and penetrate deeper into a material, the mechanisms of damage are often very similar. In an effort to efficiently take advantage of the variety of damage rates reported in the literature to obtain estimates for possible thresholds for different system, we have examined the rates of both electron induced and x-ray induced damage for a variety of materials. Based on the data, an approach is developed to compare x-ray damage rates reported for different systems and an approximate method for comparing electron beam and x-ray damage is reported. The electron beam damage is done using a 10 kV electron beam in a Phi 680 system while the x-ray damage is done in a Phi Quantum 2000. For at least some materials (e.g., poly(vinyl chloride) and poly(acrylonitrile)), the ratio of electron and x-ray damage rates are essentially identical even when the absolute rates differ by a factor of 10.

10:00am **AS-ThM6 Charge Referencing in XPS Analysis of Self-assembled Nano-phase Particle (SNAP) Surface Treatments**, *L.S. Kasten*, University of Dayton Research Institute; *V.N. Balbyshchev*, Universal Technology Corporation; *M.S. Donley*, Air Force Research Laboratory (AFRL/MLBT)

To investigate the surface chemistry of Self-assembled Nano-phase Particle (SNAP) SNAP films, X-ray photoelectron spectroscopy (XPS) was utilized to obtain detailed chemical state information on the coating constituents. SNAP coatings were created by forming nanosized siloxane structures comprised of hydrolyzed tetramethoxysilane (TMOS) and glycidoxypropyltrimethoxysilane (GPTMS) in aqueous solution and then crosslinking them upon application to form thin, dense protective organic surface treatment coatings on Al aerospace alloys. A charge referencing method from which accurate and reliable photoelectron peak binding energies could be determined was developed. In order to gain further insight into the chemical composition of the SNAP coatings, data from three related research efforts involving TOF-SIMS analysis of SNAP coatings, studies of the SNAP solution chemistry, and studies involving modeling of the SNAP oligomer formation process enabled some key assumptions to be made about the structure of the SNAP coatings. Based on these studies, an internal standard was chosen which enabled the spectra to be charge referenced, and the referenced data allowed accurate identification of chemical bonding states in the SNAP coatings. Results show that the Si bonds present in the SNAP film are a combination of the bonds in the individual precursors TMOS and GPTMS. The SNAP coatings retain the siloxane character of the of the GPTMS and TMOS precursors. These data support the concept that the nanosized siloxane macromolecules are retained through the coating application process and comprise the film. This was further verified by the use of a silicon chemical state plot, including the use of the modified Auger parameter. The SNAP film's Auger parameter value fell between the precursors' Auger parameter values. These surface analytical data are both self-consistent and consistent with the observations and assumptions of the model.

10:20am **AS-ThM7 Quantitative Depth Profiling of Silicon Oxynitride Films by Electron Spectroscopy**, *P. Mrozek, D.F. Allgeyer, B. Carlson*, Micron Technology Inc.

Detailed surface analysis was performed using X-ray photoelectron spectroscopy (XPS) and X-ray-induced Auger electron spectroscopy (XAES) on silicon oxynitride (SiON) films grown on silicon (Si). Results of conventional XPS depth profiling of SiON at shallow angles demonstrated high depth resolution with fine details of N and O distributions. Si Auger parameter analysis supplemented XPS by showing the extent of nitridization as a function of depth. Angle-resolved data were analyzed using QUASES-ARXPS software. Results are discussed in terms of possible growth mechanisms of SiON.

10:40am **AS-ThM8 Characterization of Silicon-Oxynitride Dielectric Thin Films using Grazing Incidence X-Ray Photoelectron Spectroscopy**, *E. Landree, T. Jach*, National Institute of Standards and Technology

The evolution of gate dielectric film thickness outlined in the 2002 International Technology Roadmap for Semiconductors (ITRS) is continually driving the need for new techniques sensitive to variations in spatial composition and thickness on the order of sub-nanometers. One of the promising techniques for characterizing ultrathin films is grazing incidence

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x-ray photoelectron spectroscopy (GIXPS). GIXPS utilizes the dependence on the material properties of the film, and the incident angle of the x-rays to control the electric field penetration in the sample. Varying the angle of incidence from zero to some value slightly greater than the angle for total x-ray external reflection, it is possible to probe nondestructively the chemical nature of the film at different depths. Physical properties such as depth profile, density and thickness, are extracted by comparing the calculated photoemission spectrum of a constructing model of the film structure and the measured angle dependent photoemission spectrum. The measured dielectric thin film thickness and chemical depth profile from a diverse group of silicon oxynitride samples in the range of 2 - 5 nm will be discussed. In addition, challenges associated with the dependence of the technique upon various fundamental materials parameters will be addressed. T. Jach and E. Landree. *Journal of Surface Analysis*. 9, 3 (2002).

11:00am **AS-ThM9 XPS Study of Ultrathin Ferroelectric Films**, L. Vanzetti, M. Bersani, M. Barozzi, M. Anderle, ITC-irst, Italy; V. Nagarajan, T. Zhao, R. Ramesh, University of Maryland

Lead zirconate titanate (PZT) thin films have been extensively studied for potential application in nonvolatile memory devices, infrared sensors, and microelectromechanical systems. In addition to compositional and structural factors, the impact of the thickness of the ferroelectric layer, and the interface quality have to be considered in understanding the structure-property relationship in PZT thin films. In this work we show results of our investigation on ultrathin ferroelectric films by XPS and SIMS. PbZr_{0.2}Ti_{0.8}O₃ films of varying thickness were deposited by pulsed laser deposition on SrRuO₃ buffered SrTiO₃ substrates. Ferroelectric measurements show that the switchable polarization drastically decreased as the PZT thickness is scaled down from 15 to 4 nm. XPS measurements on the two representative samples, 4 and 15nm thick, show that the composition of both films is the same. Moreover, the surface does not show ruthenium segregation from the buffer layer. This result proves that the drop in the polarization is not due to a change in the film composition. In addition, we also show SIMS depth profiling for both films.

11:20am **AS-ThM10 Auger Spectra Line Shape Study in Iron-Aluminum-Oxygen Reaction System**, S. Nayak, University of Tennessee, Knoxville; H.M. Meyer, III, Oak Ridge National Laboratory; N.B. Dahotre, University of Tennessee, Knoxville

Normalized intensity-kinetic energy Auger electron spectra were collected for different state of iron and aluminum. The standards and the samples were ion-sputtered and monitored until they attained a stable spectrum. The line-shape of spectra corresponding to iron in standard pure iron, iron oxides (FeO, Fe₂O₃ and Fe₃O₄) and Fe₃Al were compared. The spectra non-metallic irons exhibit distinctly different line shape than that of metallic iron. This change in line shape was also accompanied by shift in peak. Similarly, spectra corresponding to aluminum were collected for pure aluminum, Al₂O₃ and Fe₃Al. There is a distinct change in shape of line both in the case of aluminum and iron. The information was used to study the non-equilibrium two phenomena: (1) laser-induced reaction coating of iron oxide on aluminum alloys and (2) mechanical alloying of iron oxides and aluminum. In laser coating, the high rate of heating and cooling freeze-in the reaction between iron oxides and aluminum. Elemental mapping using the shift in peak position provides information about reaction mechanism. The spectra obtained from laser coating sample has a shape intermediate between purely metallic and oxidized iron and aluminum. The mechanically alloyed powder exhibited spectra line-shape commensurate with the extent of reaction. By choosing the window of kinetic energy, it was possible to map Fe and Al in combined and metallic state distinctly. Al₂O₃ and Fe₃Al were formed during the reaction between iron oxide and Al. The intermediate (frozen-in) reaction products showed gradual change of peak position and line shape from metallic to oxidized state for Fe and Al. The concept of line shape and peak shift was used to successfully study the reaction and its mechanism.

11:40am **AS-ThM11 The Dispersion of Quantum Well States in Cu/Co/Cu(001)**, Y.Z. Wu, C. Won, University of California, Berkeley; E. Rotenberg, Lawrence Berkeley National Laboratory; H.W. Zhao, University of California, Berkeley; N.V. Smith, Lawrence Berkeley National Laboratory; Z.Q. Qiu, University of California, Berkeley

Electrons inside a metallic thin film experience confinement in the normal direction of the film to form quantum well states (QWS) which plays a key

role in a number of important properties in metallic thin films such as the oscillatory interlayer coupling, the magnetic anisotropy, the stability of magic thickness, etc. We will report the QWS study using angle resolved photoemission spectroscopy (ARPES) for Cu/Co/Cu(100) system. QWS in the normal direction were studied for both the lower and upper bands relative to the vacuum level. The QWS in both bands can be described as a whole by the phase accumulation method (PAM). The phase shift at the interface can be obtained experimentally. The experimental value of the phase shift deviates away from the value calculated by PAM. The dispersion of QWS with different in-plane momentum was studied near the normal direction. We found that the QWS dispersion depends on the Cu film thickness and that the quantized perpendicular momentum changes with the in-plane momentum. The latter has a dramatic effect in obtaining the in-plane effective mass of the electron. The in-plane effective mass of Cu increases with the energy.

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Applied Surface Science

Room 324/325 - Session AS-ThA

Electron and Photon Spectroscopies

Moderator: R. Haasch, University of Illinois, Urbana-Champaign

2:00pm AS-ThA1 Spin Polarization Modulation through Circular Polarized Light Modulation, S. Balaz, L.G. Rosa, H.K. Jeong, P.A. Dowben, University of Nebraska, Lincoln

Spin-polarized electron sources have important applications in electron spectroscopies. Such electron spectroscopies can provide considerable insight into the spin-polarized electronic structure of magnetic materials. A variation to the spin-polarized electron gun, based on photoemission from a GaAs cathode, has been designed for spin-polarized inverse photoemission and spin-polarized electron scattering. The goal is to improve the emitted electron spin polarization by improving the control of the incident circularly polarized light, and then modulating the light polarization on the photocathode to modulate the spin-polarized photocurrent. A solid state laser, of 780 nm wavelength, in combination with a retarder was used to generate the circularly polarized light. Scheme for electron spin polarization modulations, through modulating the applied voltage to a liquid crystal retarder, we show that polarization can be modulated as well. Inclusion of such a spin-polarized electron gun as part of spin-polarized inverse photoemission and spin-polarized electron energy loss spectroscopies is discussed. D.T. Pierce, and F. Meier, Phys. Rev. B 13, 5484 (1976). F. Ciccacci, E. Vescovo, G. Chiaia, S. De Rossi, and M. Tosca, Rev. Sci. Instrum. 63, 3333 (1992). Takashi Komesu, C. Waldfried, Hae-Kyung Jeong, D.P. Pappas, T. Rammer, M.E. Johnston, T.J. Gay and P.A. Dowben, in: Laser Diodes and LEDs in Industrial, Measurement, Imaging and Sensor Applications II: Testing, Packaging, and Reliability of Semiconductor Lasers V, Edited by Geoffrey T. Burnham, Xiaoguang He, Kurt J. Linden and S.C. Wang, Proceedings of the SPIE 3945, 6 (2000).

2:20pm AS-ThA2 A PRBS-modulated TOF-HREELS Spectrometer with High Throughput and Multiplex Advantage, B.G. Frederick, Z. Yang, P. Kleban, University of Maine

We present an analysis of the factors that control the resolution, dynamic range, throughput, and multiplex advantage of a novel time-of-flight (ToF) pseudo-random binary sequence (PRBS) modulated high resolution electron energy loss spectrometer (HREELS). We describe probability based spectral estimation methods for signal recovery that achieve a throughput advantage of 100-1000, a factor of 8-16 resolution enhancement, and account for the Poisson noise distribution in the measured data. The multiplex advantage achieved depends upon a number of factors, but significantly improves upon the multiplex disadvantage expected with the conventional cross-correlation or Hadamard transform methods when the detector signal is shot-noise limited. We describe how the optical properties of the chopper affect the PRBS modulated data within a theoretical framework and utilize trajectory calculations over an analytical potential to compare with data measured on azimuthally oriented polytetrafluoroethylene (PTFE, or Teflon) films.

2:40pm AS-ThA3 Ab initio Modeling of the Vibrational Spectrum of Adsorbed Cyclopentadienyl Anion, C.M. Woodbridge, D. Kemp, Hillsdale College; D.L. Pugmire, Los Alamos National Laboratory; M.A. Langell, University of Nebraska, Lincoln

Ab initio methods have been used to model the vibrational spectrum of cyclopentadienyl (Cp), a fragment obtained from the decomposition of metallocenes, adsorbed on various substrates. In the present work, the adsorbate-substrate system was modeled using a single atom as the substrate. Vibrational frequencies, bond lengths, and bonding energies for complexes of the form $[Mn^{+}Cp^{-}]^{+}$ where $M=Ag, Ni, \text{ and } Si$ have been computed. The complexes were constructed to model two different orientations of the adsorbed Cp ring: one where the plane of the Cp ring is parallel to the surface normal and the other where the plane is perpendicular to the surface normal. The computed vibrational frequencies have been compared to vibrational losses observed in HREEL spectra of Cp, produced from the decomposition of nickelocene, adsorbed the Ag(100), Ni(100), and Si(111)- 7×7 substrates. Despite the relative simplicity of the model, the calculated vibrational frequencies are in good agreement with the HREEL spectra.

3:00pm AS-ThA4 Photon Angle Dependence of Plasmon Loss Measured by the Double Angular Photoelectron Integrated Analyzer System, A. Tanaka, ULVAC-PHI, Inc., Japan; H. Yoshikawa, NIMS, Japan; M. Kimura, SPring-8 Service, Japan; S. Fukushima, NIMS, Japan

Plasmon loss peaks associated with photoelectron peaks from the silicon specimen is measured. The analyzer and the specimen are tilted simultaneously with maintaining the emission angle constant. This tilting effectively changes the incident angle of photons to the specimen. The angle of photon incidence was ranged from 35 to 90 degree. It caused a change of relative intensity of 1st plasmon loss peaks to the original photoelectron peaks. Photon energy was chosen to match the Si 1s photoelectron energy at the Si 2s energy excited by Mg K α x-ray. Ellipsoidal undulation is applied for the synchrotron radiation to simulate the x-ray used for X-ray photoelectron spectroscopy. 3 loss peaks generated by Si 1s, Si 2s and Si 2p are compared. The plasmon loss ratios to mother peaks approximately 10% reduced according to the angle of incidence for all of these spectra, and reduced more at the total reflection conditions. Only for total reflection conditions, this result shows the limitation of excitation range close to the surface, as the energy loss zone becomes smaller comparable with electron inelastic mean free paths. However, this phenomenon is different from surface effect as the emission angle was kept constant at $0\pm 2^\circ$ and acceptance angle of the analyzer smaller than 10° . When we require precise quantification, we have to consider energy loss process generated in deeper range, too.

3:20pm AS-ThA5 Photon, Electron, and Ion Spectroscopies Applied to Thin Strained Si Films, S. Zollner, R. Liu, M. Canonico, M. Kottke, Q. Xie, S. Lu, M. Sadaka, T. White, A. Barr, B.-Y. Nguyen, S. Thomas, Motorola; C.S. Cook, Arizona State University; A. Volinsky, Motorola

Applied thin-film spectroscopies can be classified by the primary (incident) and secondary (scattered, specularly reflected, diffracted) particle (photon, electron, ion) and by the energy loss (elastic, inelastic) of the interaction. The term spectroscopy implies that the energy of the primary and/or secondary particle is well-known, measured, or varied. We describe applications of various thin-film spectroscopies to thin (15-20 nm) Si layers under tensile biaxial stress, grown pseudomorphically on thick relaxed Si $_x$ Ge $_x$ buffer layers. Such Si layers have higher electron and hole mobilities than regular bulk Si and are therefore considered for next-generation CMOS technologies. Particular emphasis is placed on the physical mechanism of each spectroscopy technique, the results obtained (thickness, composition, stress), and the potential shortcomings. Specifically, we use UV Raman spectroscopy (325 nm laser excitation) to determine the strain in the Si layer from the frequency shift of the Si-Si lattice vibration. The contributions of the tensile hydrostatic strain and the compressive shear strain to the E1 peak shift (near 3.4 eV) cancel almost exactly, therefore ellipsometry cannot be used to determine strain. However, the piezo-optical effects are significant enough to make ellipsometry unreliable for the determination of the Si thickness or the Ge content of the alloy buffer. Piezo-optical effects are not an issue for x-ray reflectivity, since the dielectric constant of most materials is very close to unity for Cu K α radiation, but surface roughness can be a problem. We also discuss results from secondary ion mass spectrometry and Auger electron spectrometry to determine composition of the layers.

4:00pm AS-ThA7 Insights into the Physical and Electronic Structure of Surfaces from Reflection Anisotropy Spectroscopy, P. Weightman, University of Liverpool, UK

Reflection Anisotropy Spectroscopy (RAS) is a non destructive surface sensitive optical probe capable of operation within a wide range of environments. RAS achieves surface sensitivity by measuring the change in polarisation on reflection of normal incidence light from the surface of a cubic crystal. The technique has been shown to be a sensitive probe of molecular orientation on surfaces, which is capable of monitoring growth at metal/liquid interfaces. Recent improvements in instrumentation have greatly increased the speed of response of RAS equipment so that it can be used to monitor growth at realistic growth rates and to provide information on the orientation and interaction between biological molecules at metal/liquid interfaces on a fast time scale. This talk will present recent results of studies of the physical and electronic structure of metal and semiconductor surfaces and of the RAS of DNA bases and DNA sequences adsorbed at the Au(110)/electrolyte interface. A brief description will be given of how the sensitivity, spectral range and in particular the timescale of RAS will be radically improved by the proposed UK Fourth Generation Light Source (4GLS).

Thursday Afternoon, November 6, 2003

A.I. Shkrebtii and R. Del Sole, Phys. Rev. Lett. 80 3133-6 (1998).@footnote 2@B.G. Frederick, J.R. Power, R.J. Cole, C.C. Perry, Q. Chen, S.Haq, Th. Bertrams, N.V. Richardson and P. Weightman. Phys. Rev. Lett. 80 4490-3 (1998).@footnote 3@B. Sheriden, D.S. Martin, J.R. Power, S.D. Barrett, C.I. Smith, C.A. Lucas, R.J. Nichols and P. Weightman, Phys. Rev. Lett. 85 4618-21 (2000).@footnote 4@P. Harrison, T. Farrell, A. Maunder, C.I. Smith and P. Weightman, Meas. Sci. Technol. 12 2185-91 (2001).

4:40pm **AS-ThA9 Spectroscopic Ellipsometry Analysis of Chemical Vapor Deposited Zirconia Thin Films, B.R. Rogers, Z. Song, R.D. Geil, D.W. Crunkleton, Vanderbilt University**

The integration of high-k dielectric materials into MOSFET fabrication processes will require a non-destructive, fast, and accurate method for film characterization and process control. Spectroscopic ellipsometry (SE) is an outstanding candidate for these applications. This study reports the results of a multi-sample, variable-angle SE (VASE) analysis to characterize zirconia thin films deposited on Si(100) by high vacuum chemical vapor deposition (HVCVD). We evaluated several optical models of the samples to determine which best described the experimental data. A two-layer model consisting of a Tauc-Lorentz layer on the top of a Lorentz interfacial layer resulted in the best fit. This model was used to extract the optical constants of both the zirconia and the interfacial layers. The extracted optical constants were then used as constants in additional models to optimize the analyses. Most of the models fit the data below 6.0 eV extremely well. However, significant differences in goodness of fit were seen between the models' predictions above 6.0 eV photon energies. We feel these differences are due to an increased sensitivity to the interfacial layers for photons above 6.0 eV. The influence of the quality of interfacial layers on the accuracy of extracted optical constants will be discussed. Supporting data from XPS, TEM, and time-of-flight medium energy backscattering analyses will also be presented.

5:00pm **AS-ThA10 Surface Vibrational Spectroscopy Beyond the Harmonic Approximation: On the Selection Rules of Binary Modes, P.E: Uvdal, M. Andersson, Lund University, Sweden**

Vibrational analysis of surface adsorbates involves in general the assignment of fundamental normal modes. Based on such assignment conclusions about chemical identity and geometry can be drawn. It is however well known from fundamental textbooks on molecular vibrations that if one goes beyond the harmonic approximation of the intramolecular bond potential overtone and combination modes are allowed. Binary modes, i.e. excitation of one vibration with two quanta or excitation of two vibrations with one quanta, will be the most intense even though higher excitations are allowed. The presence or absence of binary modes will contain information about bond anharmonicity and coupling between different modes. The selection rules, that is the absence/presence of them will be discussed based on recent first principle calculations.@footnote 1@ @FootnoteText@ @footnote 1@M.P. Andersson and P. Uvdal, Phys. Rev. Lett. 90 (2003) 076103.

Applied Surface Science

Room 324/325 - Session AS-FrM

SIMS

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

8:20am AS-FrM1 Static ToF-SIMS - A VAMAS Interlaboratory Study, 2002, I.S. Gilmore, M.P. Seah, National Physical Laboratory, UK

The first VAMAS static SIMS inter-laboratory study was conducted by NPL in 1996. That study included 21 static SIMS instruments with a wide variety of spectrometer types. Results indicated that, whilst repeatabilities could be as good as 1%, they were on average only 10%. Additionally, the equivalence of data between all the different instruments was improved by a factor of 4 by use of a relative instrument transmission function RISR. In 2002, the second VAMAS static SIMS inter-laboratory study was conducted, this time restricted to time-of-flight instruments which now dominate static SIMS analysis. The principal objectives are (i) to determine the repeatability of instruments, (ii) to determine the reproducibility of between laboratories, (iii) to evaluate variations in spectral response between different types of SIMS instruments and, optionally, (iv) instrument compatibility with G-SIMS may also be tested. Data have now been received from 31 laboratories (10 with G-SIMS data) from 16 countries. Three reference materials were used in this study, a thin spin cast polycarbonate film, a thin layer of polystyrene oligomers on silver and PTFE. A protocol for analysis was supplied to each laboratory. Relevant details of the protocol will be discussed. Excellent repeatabilities have been demonstrated with over 90% of participants achieving average repeatabilities of better than 5% and 30% of participants with better than 1.5%. The reference materials give an average repeatability of 2% over 27 laboratories. This shows a considerable improvement from the average repeatability of 10% in the former study. An analysis of the results and the issues of conducting both SSIMS and G-SIMS using different instruments will be presented. I S Gilmore and M P Seah, Surf. Interface Anal., 29 (2000) 624. I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000) 465.

8:40am AS-FrM2 TOF-SIMS with Polyatomic Primary Ion Bombardment: A Comparison Between Different Projectiles, R. Möllers, F. Kollmer, D. Rading, M. Terhorst, E. Niehuis, ION-TOF GmbH, Germany; R. Kersting, B. Hagenhoff, Tascon GmbH, Germany

In the past TOF-SIMS has been established as an analytical technique for the chemical characterization of surfaces. In particular the simultaneous detection of atomic as well as molecular ions, and the ability to obtain these information laterally resolved, makes this technique well suited for the analysis of structured molecular surfaces. Recently it was shown that polyatomic primary ion bombardment (e.g. SF₅⁺, C₆₀⁺, Au_n⁺-clusters,...) leads to a considerable enhancement of the secondary ion emission efficiency for organic materials. This enhancement not only increases the sensitivity for molecular species up to several orders of magnitude, but also pushes the useful lateral resolution in organic imaging down to the sub- μ m range. In this presentation we will continue our systematic investigation on the influence of different primary ion species, including monoatomic as well as polyatomic primary ions, on secondary ion parameters such as yield Y, damage cross section σ , efficiency $E = Y/\sigma$, and useful lateral resolution Δ . Those parameters have been evaluated for a variety of different sample materials and sample preparations. Also the effect of different primary ion energies (4 to 25 keV) will be issued. The results from this investigation will be expanded by examples from routine analysis in a commercial service laboratory.

9:00am AS-FrM3 Characterisation of Peptides Using TOF-SIMS with Polyatomic Primary Ion Bombardment, K. Pfitzer, E. Tallarek, R. Kersting, B. Hagenhoff, TASCAN GmbH, Germany

In the 80s of the last century it could be shown that the optimum sample preparation for SIMS of peptides under monoatomic primary ion bombardment is a monolayer preparation on noble metal substrates. Yields from thick overlayers turned out to be distinctly lower compared to the monolayer preparation. Although many applications were possible by this type of preparation, information could not be gained from biological material directly where peptides or proteins are embedded in thick organic matrices. Now, the use of polyatomic primary ions offers new opportunities. Under such primary ion bombardment conditions molecular ions can be emitted with high secondary ion formation efficiency also from thick organic layers. Efficiency

enhancement factors can reach up to 3 orders of magnitude. We have applied Ga⁺, Au₁⁺, Au₂⁺, Au₃⁺ as well as Au₅⁺ bombardment to several peptides. The peptide masses varied from 1000u up to 3500u. Variations of the chemical structure could be tested by varying the number of basic and acidic side chains. The samples were prepared as monolayers on noble metal substrates, as thick overlayers (powders, thick layers spin coated from solutions) as well as mixed into nitrocellulose. The results show that polyatomic primary ion bombardment indeed allows to desorb peptides efficiently from thick layers. Progress can therefore be expected for SIMS imaging of peptides and proteins in biological matter. References: A. Benninghoven; J. Vac. Sci. Technol. A3 (3), (1985), 451 D. van Leyen, D. Greifendorf, A. Benninghoven in: A. Benninghoven, A. M. Huber, H. W. Werner (eds.); Secondary Ion Mass Spectrometry (SIMS VI); John Wiley & Sons, Chichester, 1988, 679 D. Stapel, M. Thiemann, B. Hagenhoff, A. Benninghoven, in: A. Benninghoven, P. Bertrand, H. N. Migeon, H. W. Werner (eds.); Secondary Ion Mass Spectrometry (SIMS XII); John Wiley Sons, Chichester, 2000, 255

9:20am AS-FrM4 SIMS Quantification for Depth Profiling: Overview, Recent Results for Surfaces and Insulators, and Current Problems, F.A. Stevie, C. Gu, A. Pivovarov, D.P. Griffiths, North Carolina State University; J.M. McKinley, NanoSpective; H. Francois-Saint-Cyr, University of Central Florida

INVITED

This paper provides an overview of quantification for SIMS depth profiling and presents recent results illustrating the importance of surfaces, matrix variations, and insulators on the quantification process. Quantification is complicated by the orders of magnitude variation of secondary ion yields over the periodic table and significant variation of these ion yields for different matrices. Since practical methods for calculation of elemental sensitivity factors using theoretical methods do not exist, a standard for each element in the matrix in which it is contained is required. However, only a few standards with high accuracy have been produced. Despite these limitations, measurement precision less than 1% can be achieved. Using ion implant standards, quantification can be achieved at surfaces, within multilayered samples, at interfaces, and in bulk materials. Implantation through a removable layer provides a known quantity at a surface that can be used as a standard by many analytical techniques. Multiple layers require an understanding of each layer. A study of O₂⁺ SIMS analysis of TaN/Ta barrier penetration by Cu shows the low secondary ion yield in the barrier compared with the SiO₂ and Si regions complicates interpretation. Insulators present additional problems due to sample charging. Analysis of thin insulating films can be performed by using electrons with energy sufficient to penetrate the layer thus rendering the layer conductive. Magnetic sector SIMS analysis of GaN structures can be aided by the use of molecular secondary ions accompanied by the maximization of mass spectrometer secondary ion energy bandpass. Adequate O⁻ primary beam density can be obtained to provide depth profiles in bulk insulators. Many aspects of quantification using SIMS still require additional study. It is difficult to extend the information from one matrix to another, and analysis of insulators such as porous low-k dielectrics present special problems.

10:40am AS-FrM8 SIMS Backside Depth Profiling of Test Pads on PMOS Patterned Wafers, E.S. Windsor, J.G. Gillen, P.H. Chi, National Institute of Standards and Technology; J.A. Bennett, International Sematech

In semiconductor electronics, the diffusion of elements from one layer to another can lead to poor performance or device failure. Interlayer diffusion is of particular interest in process design where experimentation with films of varying composition and thickness is common. In this study, we investigate a patterned PMOS wafer containing hafnium oxide as an experimental gate dielectric. The question arises as to whether boron from the overlying polysilicon layer has diffused through the dielectric down into the silicon substrate below. We use Secondary Ion Mass Spectrometry (SIMS) to investigate possible boron diffusion because of the high analytical sensitivity and excellent depth resolution of the SIMS technique. Front-side SIMS analyses of these patterned wafers can be limited by: (1) difficulty sputtering patterned (non-planar) surfaces, (2) initial or sputter induced topography of the sample surface and (3) degraded depth resolution caused by ion mixing when sputtering from high to low concentrations of the element(s) of interest. To minimize these effects, it is often desirable to sputter (analyze) from the backside of the wafer. Backside analysis requires the removal of the majority of the silicon substrate (final substrate thickness less than 1 micron). This is accomplished by mechanical grinding and polishing. Since the features of interest (test pads in this study) can not

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be observed from the backside, they must be marked from the front side prior to mechanical preparation. Marking is accomplished by ion sputtering, and we sputter both holes and raster craters. Holes mark the features of interest while the larger raster craters are used to aid thickness determinations and adjust planarity during mechanical preparation. Also investigated are factors that limit the usefulness of mechanical backthinning preparation such as polished surface roughness and sample polishing planarity.

11:20am **AS-FrM10 Development and its Application of Multiple as Delta Layer Si Reference Thin Film for Shallow Junction SIMS Profiling**, *D.W. Moon*, Korea Research Institute of Standards and Science, South Korea; *H.K. Kim, K.J. Kim*, Korea Research Institute of Standards and Science; *H.K. Shon, J.Y. Won, J.C. Lee*, Samsung Advanced Institute of Technology, Korea; *F. Toujou*, Matsushita Technoresearch, Inc., Japan

To meet the demand for shallow junction SIMS profiling, the surface transient Si sputtering effect should be corrected in addition to the improvement of depth resolution. With low energy grazing incident ions, the SIMS depth resolution could be improved better than 1 nm. For the correction of the surface transient effect, we report that multiple As delta-layer Si thin films characterized with HRTEM and MEIS can be used as a reference thin film. With the reference thin films, the depth scale shift in the surface transient region can be calibrated under each analysis condition. For low energy O_2^+ and Cs^+ ion bombardment, the average Si sputtering yield in the first surface 5 nm layer can be 50~70% higher than that in the steady state for typical incidence angles around 45°. However, for incidence angle above 60°, the surface transient effect enhanced significantly with the increase of the sputtering yield up to 150% and the extension of the surface transient region up to 15 nm for low energy Cs^+ bombardment. Preliminary understanding for the enhanced surface transient effect will be discussed.

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