Applied Surface Science Division
Room 6A - Session AS-MoM
Imaging and Small Area Analysis

Moderator: J.E. Fulghum, Kent State University

8:20am **AS-MoM1 Reading Mechanism Evaluation on Detection of Spontaneous Polarization in a PZT Thin Film***, **W. Moon,*** Pohang University of Science and Technology, Republic of Korea*; H. Shin, J. Lee, K. Lee, Y.E. Pak,* Samsung Advanced Institute of Technology, Republic of Korea

The methods for detecting a small polarized area in a PZT thin film by SPM techniques are investigated theoretically and experimentally. A small polarized area in a PZT thin film can be constructed and detected by use of SPM. It is found that a 4 µ m by 4 µ m polarized area can be more easily detected by use of EFM techniques under contact-mode-AFM operation. It is shown experimentally as well as theoretically that effects of electrostatic forces are dominant for detection signals for polarized domains in a PZT thin film compared with piezoelectric vibration effects.

8:40am **AS-MoM2 A New Variable Temperature Beam-Deflection AFM***, A. Feltz, **P. Güthner**, T. Berghaus,* OMICRON Vakuumphysik GmbH, Germany

AFM experiments at variable temperature are very important for the investigation of phase transitions, growth behaviour, surface diffusion and other temperature depending processes on insulating surfaces with atomic resolution. For this purpose a new Variable Temperature AFM has been developed for minimum drift over a wide temperature range, i.e. AFM operation from 25 K to more than 1000 K. The special optical setup allows to realize a scanned-tip instrument. This allows to limit heating and cooling to the sample realizing a wide temperature range and low drift even for fast temperature changes. The beam deflection technique allows simultaneous topography and lateral force imaging in contact mode, non-contact mode AFM with true atomic resolution, as well as Magnetic Force Microscopy (MFM) and Electrostatic Force Microscopy (EFM). Au(111) was used to study friction at low temperatures. Images of the gold (111) surface in contact mode show the atomic structure and the 23 x @sr@3 surface reconstruction in the topography, and the friction image. At low temperatures down to 30 K the atomic scale friction is drastically increased. True atomic resolution has been achieved in dynamic mode images of silicon (111) 7x7 over a temperature range from 50 K up to about 1000 K. Silicon cantilevers prepared by sputter cleaning of the tip were used for these images. Further experiments will be performed on a non-conducting sample (NaCl).

9:00am **AS-MoM3 AFM Imaging of Thermal Phase Transitions in Polymers***, **S.N. Magonov,*** Digital Instruments **INVITED**

Atomic force microscopy (AFM) became the leading scanning probe technique, which is used in semiconductor, data storage, and plastics industries. AFM is routinely applied for examination of polymer materials at ambient conditions. Its validity for high-resolution real-space visualization of polymer morphology and nanostructure as well as for compositional mapping of heterogeneous systems had been already recognized. AFM substantially complements other microscopic and diffraction techniques providing visualization of single macromolecules and crystalline polymers, mapping of rubber domains with different cross-linking density and non-destructing imaging of sub-surface features of viscoelastic materials at depths from a few to hundreds of nanometers. Examination of structural changes at thermal transitions is a relatively new AFM capability. Several examples demonstrating such applications will be discussed in this contribution. They include monitoring of structural changes in mesomorphic polysiloxanes, thermal reorganization in block copolymers and visualization of melting and crystallization in ultrathin (20 nm) films of polyolefines.

9:40am **AS-MoM5 Geometry and Tip Effect Simulation in Scanning Kelvin Probe Microscopy***, **A.E. Efimov,*** Silicon-MDT Ltd., Russia*; S.R. Cohen, I. Visoly, D. Cahen,* Weizmann Institute of Science, Israel

Scanned probe microscopy (SPM) techniques have become an integral part of the fabrication and study of miniaturized devices, as well as of nm-scale features in general. Well-known geometric effects of tip size have been studied and several solutions were proposed for their removal from obtained topographical images. A more subtle effect exists for electronic surface mapping using such modes as scanning Kelvin probe microscopy (SKPM). These effects become significant for high resolution work on surfaces whose topography is not flat. We demonstrate this phenomenon on SKPM studies of CdTe films which exhibit both rich topography and electronic structure at grain boundaries. II-VI semiconductors exhibit interesting electronic properties which not only allow their applications in miniaturized electronic device structures, but suggests their study as model systems as an end in itself. A combined theoretical and computational approach is used to simulate the SKPM imaging process, calculate geometric contributions and separate electronic features from geometric distortions in the scanned probe images, in an attempt to recover the surface potential and therefore move towards true SKPM imaging. The results are compared with parallel techniques, such as scanning tunneling spectroscopy (STS), where the geometric contributions can be effectively ignored.

10:00am **AS-MoM6 Imaging of Particulates using Auger Electrons***, **M. Prutton**, D.K. Wilkinson, M.M. El Gomati, M. Jacka, M. Kirk,* University of York, UK **INVITED**

The currently favoured methodology of scanning Auger microscopy uses UHV SEM systems equipped with field electron emission sources in the column and coaxial mirror or concentric hemispherical electron energy analysers to detect electrons of a selectable kinetic energy. One technological objective is to produce digital maps in which the pixel intensities are proportional to the atomic fractions of the element giving that Auger line in the electron spectrum. This is significantly more difficult than simply acquiring and displaying signals proportional to the height or area of that Auger line because of the dependence of the Auger yield upon the local angle of incidence, the varying composition of sub-surface material and the presence of sharp changes in composition in the vicinity of the current pixel. Most of these difficulties have been removed or minimised in the York Auger microscope (MULSAM). The principal features of MULSAM will be outlined together with a short introduction to the methodology used to combine images obtained from several different scattered electron detectors around the sample. Examples will be given for correction of topographical artefacts in chemical maps and the use of multi-variate statistics to assist in the analysis of particulate catalysts. One disadvantage of current SAM designs is that sequential data acquisition is slow for multi-element samples. A new hyperbolic field analyser (HFA) will be reported that can acquire simultaneously an entire 1024 channel spectrum. It opens the way to obtain entire spectra in each pixel of an image. This could lead to very powerful methods of surface microanalysis using different parts of the spectrum in each pixel to correct for the local topographical and sub-surface composition. Some examples of spectra obtained from particulates using an HFA will be given. The outline design of a spectrum-imaging Auger microscope (SISAM) will be presented.

10:40am **AS-MoM8 Functionalised Plasma Polymer Coatings for Improved Durability of Aluminium-epoxy Adhesive Joints***, **B.J. Tielsch,*** Kratos Analytical, UK*; M.R. Alexander, G.E. Thompson,* The Corrosion and Protection Centre, UMIST, UK*; T.M. Duc,* BIOPHY Research S A, France*; E. McAlpine,* Alcan International, UK

There is much interest in the use of plasma polymer (PP) coatings to promote adhesion and/or inhibit corrosion of metals.@footnote 1@ These offer environmental and performance benefits over conventional "wet" processing methods such as chromic acid anodising (CAA). Here, we explore the use of carboxylic acid functionalised PP as an adhesion promotion coating on aluminium. The acid functionality, retained from the monomer structure in the plasma deposition process, is intended to form stable chemical bonds with both the aluminium oxide/hydroxide surface and epoxy based adhesives.@footnote 2@ Plasma polymerised acrylic acid and a plasma co-polymer of acrylic acid and octadiene, have been deposited onto plasma etched AA6016 aluminium alloy using RF deposition apparatus. An amine hardened epoxy-based adhesive formulation has been used to bond single lap shear (SLS) joints of PP-coated and CAA alloy. Combining tensile testing of SLS joints with locus-of-failure determination from imaging-XPS and TEM, the relative success of the pretreatments can be gauged. Joint durability was probed by testing joints after storage in water at 60 °C. A decrease in joint strength upon ageing was accompanied by a visual change from failure in the adhesive to failure at a near interfacial region. Chemical state differences in the XPS C1s core level between the acid containing PP and the epoxy containing resin were imaged over the fracture surface. This allowed the effect of PP deposition conditions upon the locus-of-failure and the relationship between this and the failure load to be investigated. Furthermore, information on the distribution of the amine hardener was obtained by imaging of the nitrogen peak. TEM examination of sections taken from the fracture surfaces was correlated with the information obtained using imaging XPS. @FootnoteText@ @footnote 1@R.H. Turner, I. Segall, F.J. Boerio, G.D.

Davis, J. Adhesion 62, p. 1 (1997) @footnote 2@M.R. Alexander, S. Payan and T.M. Duc, SIA 26 p. 961 (1998).

11:00am **AS-MoM9 Glass Transition at Film Surfaces of Polymer Blends with Nanometer Spatial Resolution*, F. Dinelli,*** University of Washington, US*; C. Buenviaje,* University of Washington*; M. Rafailovich,* State University of New York at Stony Brook*; R.M. Overney, R. Luginbuhl,* University of Washington*; J. Sokolov, X. Hu,* State University of New York at Stony Brook

Surface structure and properties of thin polymeric films are of crucial interest for many technological applications. In ultrathin polymer films we have found that interfacial interactions and local confinement alter the physical properties. Recently we have shown that the glass transition temperature at the surface of thin films can be accurately measured using shear modulation atomic force microscopy (AFM). In this paper we present a first application of this technique to polymer blends (PS/PBMA and PS/PMMA) which, depending on the film thickness and the local spinodal decomposition, offer quite complex folded interfacial regimes. In particular we will present profiles of the glass transition temperature across phase boundaries as a function of film thickness, relative composition and degree of mixing.

11:20am **AS-MoM10 Laser-SNMS and TOF-SIMS Characterization of Sub-µm Structures*, R. Kamischke*,** *F. Kollmer, A. Schnieders, A. Benninghoven,* Universität Münster, Germany

Sputtering based surface mass spectrometry, as SIMS or Laser-SNMS, combines high sensitivity with high lateral resolution, provided a high fraction of sputtered particles is ionized and a fine focused primary ion beam is applied. Whereas for molecular samples static SIMS is the technique of choice, element analysis can be achieved in addition by dynamic SIMS and by postionization of sputtered neutrals (SNMS). In sub-µm characterization the total amount of material available for an analysis is extremely small. Therefore the transformation probability of a surface atom into an ion should be optimized. The large fraction of sputtered neutrals and their efficient laser-postionization results in a high Laser-SNMS sensitivity. The use of a time-of-flight (TOF) mass spectrometer guarantees parallel mass registration at high transmission. In this contribution we report on recent results of TOF-SIMS and Laser-SNMS characterization of AFM tips (Si@sub 3@N@sub 4@ as well as Si after surface modification or metal loading, respectively) and of sub-µm particles, ranging in size down to 15 nm. The main intention of our investigations was to find out the limits in sensitivity for these two surface mass spectroscopies and to compare both techniques. All experiments were carried out in a gridless reflectron based time-of-flight instrument equipped with a fine focused Ga+ source (< 80 nm) and an excimer laser (248 and 193 nm) for nonresonant postionization. The instrument allows a direct comparison of SIMS and Laser-SNMS results of the same sample. We succeeded in chemical characterization of surface structures (nanotips as well as particles) down to the 10 nm scale by both techniques. Useful yields achieved in SIMS and Laser-SNMS reach 10@super -3@ and 10@super -2@, respectively. As a general result we found that the characterization of the elemental composition of structures with dimensions well below the spot size of the primary ion beam is possible.

Applied Surface Science Division
Room 610 - Session AS1-MoA

Molecular Mass Spectrometry including Interpretation

Moderator: S.J. Pachuta, 3M

2:40pm **AS1-MoA3 Interpretation of Static SIMS Spectra**, ***D. Briggs,*** Siacon Consultants Ltd., U.K. **INVITED**

Static SIMS has rapidly developed into a powerful tool for the molecular characterisation of surfaces, with modern time-of-flight (ToF) instruments capable of providing both high mass resolution (m/@DELTA@m >7000)and high spatial resolution (~ 0.1 micron). Although most of the emphasis to date has been in the application to organic/polymeric systems the technique has equal potential for the surface characterisation of inorganic materials. However, the information content of ToFSIMS spectra is enormous and the interpretation of 'unknown' spectra consequently poses a serious challenge. There is a widespread feeling that the full exploitation of the technique is limited by interpretation problems, particularly with the pressure to deskill/automate all analytical operations. Compared with other forms of mass spectrometry and especially EI-MS, SIMS presents extra problems for spectral interpretation: the physical basis of the ion formation process is very poorly understood, the spectra are influenced by the primary ion used and by the matrix from which the ions originate and there are no established 'rules' for fragmentation. The development of searchable databases of standard spectra has been a key feature of other molecular spectroscopies and this approach clearly represents a way forward for SIMS. Aspects of the development of the only stand-alone database@footnote 1@ will be discussed in the light of these issues. @FootnoteText@ @Footnote 1@The Static SIMS Library, SurfaceSpectra Ltd, Manchester, UK

3:20pm **AS1-MoA5 Characterization of Polymer Additives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)**, ***R. Kersting,*** TASCON GmbH, Germany; *R. Verlaek,* DSM Research, The Netherlands; *B. Hagenhoff,* TASCON GmbH, Germany; *A.P. Pijpers,* DSM Research, The Netherlands; *B.C. Schwede,* ION-TOF GmbH, Germany

Polymers used for industrial purposes generally contain various additives to improve the product performance. Substance classes include anti-oxidants, plasticizers and flame retardants. Typical concentrations are in the order of some 100 to 1000 ppm. Although much is known about the bulk composition of the additive containing polymer not many information on the surface composition of real industry polymers is available. Generally, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is an ideally suited analytical technique to characterize the surface composition because it offers detailed molecular information with high sensitivity. On the other hand the surface concentration in real world systems can be very small, even below the detection limit of normal TOF-SIMS analysis. Therefore most TOF-SIMS studies of polymer additives have concentrated on pure materials or highly concentrated model systems. Recently, we have started a systematic study on the secondary ion emission behaviour of polymer additives using model systems containing the additives in their normally applied concentrations and embedding them into their normal host polymer. The study aims at the automated identification of additives in real world samples from their TOF-SIMS spectra. Special emphasis is therefore laid on the emission pattern for use in a spectra library and the determination of detection limits. Different primary ion bombardment conditions (monoatomic primary ions: Ar@super +@, Ga@super +@; polyatomic primary ions: SF@sub 5@ @super +@) were used to study the influence of primary ion mass and polyatomicity on the secondary ion emission. We will present our first results obtained on antioxidants. Whereas most substances can be analyzed to satisfaction using primary ions like Ar@super +@ or Ga@super +@, it turned out that in some cases polyatomic primary ions (SF@sub 5@ @super +@) had to be used in order to reach acceptable detection limits.

3:40pm **AS1-MoA6 Secondary Ion Emission from LB-Layers Under Molecular Primary Ion Bombardment**, ***D. Stapel,*** *M. Thiemann,* Universität Münster, Germany; *B. Hagenhoff,* TASCON GmbH, Germany; *A. Benninghoven,* Universität Münster, Germany

Secondary ion yields Y(X@sub i@@super q@) increase considerably when changing from atomic to molecular primary ions, whereas the simultaneous increase in the corresponding damage cross section @sigma@(X@sub i@@super q@) is much smaller. This holds in particular for thick molecular samples like LB multilayers or polymers. For LB multilayers we found yield increases up to a factor of 1000, when changing from Ar@super +@ to SF@sub 5@@super +@ bombardment. This phenomenon is important for practical analytical applications of TOF-SIMS, because yields, damage cross sections, and the resulting ion formation efficiencies E=Y/@sigma@ determine the achievable sensitivity as well as the achievable lateral resolution. The secondary ion emission of well defined model LB systems were investigated for a more detailed understanding of the complex sputtering and ion formation processes especially under different molecular primary ion bombardment. We investigated three series of LB layers (n=1, 3, 5, 7 ; n : number of monolayers) under 1 - 10 keV O@super +@, Ne@super +@, Ar@super +@, Xe@super +@, O@sub 2@@super +@, CO@sub 2@@super +@, SF@sub 5@@super +@, C@sub 7@H@sub 7@@super +@, C@sub 10@H@sub 8@@super +@, C@sub 6@F@sub 6@@super +@ and C@sub 10@F@sub 8@@super +@ bombardment. Y(X@sub i@@super q@) as well as @sigma@(X@sub i@@super q@) were determined. Our experimental results demonstrate a more pronounced yield and efficiency enhancement for multilayers (n>1). The increase in Y, @sigma@ and E features a saturation behaviour for molecular primary ion species containing more than 6 atoms. We could not find an influence of the chemical composition of the primary ion (SF@sub 5@@super +@/C@sub 7@H@sub 7@@super +@ e.g.) on this enhancement under static SIMS conditions. We compared the secondary ion and secondary neutral emission depths under atomic and molecular primary ion bombardment, and determined the influence of primary ion energy on secondary ion emission.

4:00pm **AS1-MoA7 Enriched Spectral-information from TOF-SIMS Spectra of Self Assembled Monolayers: More Than Just Molecular Ions**, *D.J. Graham,* ***B.D. Ratner,*** University of Washington

Engineered biomaterials that accurately trigger complex biological processes such as healing require complex surface modifications. This increase in complexity must be met by equally capable surface analysis tools such as TOF-SIMS. To extract information from complex organic surfaces, one should consider the spectrum as a whole, instead of selecting only a few key peaks. This study demonstrates that the information content of a TOF-SIMS spectrum does not reside solely in the molecular and cluster ions, but that each region of the spectrum contains enough information to clearly distinguish the samples. For this study dodecanethiol self-assembled monolayers (SAMs) were prepared from 0.01mMol solutions in ethanol for different times (2sec,1min,5min,15 min,30 min,1hr,24hr,6d). Principal component analysis (PCA) models from the TOF-SIMS negative and positive spectra were constructed using the entire data set and from partial data sets from mass ranges m/z=0-100,100-200,200-300,400-500,500-1000. Scores plots from the PCA models show that data from each set were able to distinguish the samples. Regions containing the molecular ions showed enhanced ability to distinguish the samples. In the overall model it was seen that there is a relative increase in the intensity of low mass hydrocarbon fragments (C to C3) with increasing time. Similar trends were seen in the positive spectra where a relative increase of C to C4 hydrocarbon fragments was seen with increasing time. This increase was accompanied by a decrease in the intensity of C5 and above hydrocarbon fragments. This data suggests that as the SAM surface becomes more ordered and crystalline, the emission of longer fragments from the thiol chains is reduced relative to the emission of short fragments. As there is also an enhancement of the emission of the thiol head group ion, it is believed that these short fragments arise by the clipping of the tops of the assembled layer by the primary ion or energetic secondary ions.

4:20pm **AS1-MoA8 Static SIMS with Polyatomic Primary Ions**, ***A. Benninghoven,*** *D. Stapel, O. Brox, B. Burkhardt, H.F. Arlinghaus, C. Crone, M. Thiemann,* Universität Münster, Germany

Polyatomic primary ion bombardment results in an increase in secondary ion yields Y and damage cross sections @sigma@ in such a way that the ion formation efficiency E = Y/@sigma@ increases. Investigated samples include metal and semiconductor surfaces (Ag, Si, GaAs) in different oxidation states, bulk and spin coated polymers with additives (PET, PC, PI, PP, PTFE, PMMA, PEG), SA- and LB - mono and - multilayers (thioles, arachidic acid on Au, PMA on Ag), hydrocarbon contamination layers on Si and GaAs, monolayers of biomolecules on Ag and other substrates, and biopolymers, technical polymers and pharmaceuticals isolated in an organic matrix. They have been bombarded by a variety of primary ions in the keV range O, Ne, Ar, Xe, O@sub 2@, CO@sub 2@, SF@sub 5@, C@sub 7@H@sub 7@, C@sub 10@H@sub 8@, C@sub 6@F@sub 6@ and C@sub 10@F@sub 8@. For atomic primary ions we found an increase in secondary ion yields with increasing mass of the primary ion, but only relatively small increases in efficiency. Compared with atomic ion bombardment, molecular primary ion bombardment always results in a yield and efficiency enhancements. No significant influence of the chemical composition of the primary ions on secondary ion yields has been observed, as long as static SIMS conditions were met. Yield and efficiency enhancements show saturation behaviour for primary ions composed of more than 6 (heavy) atoms. We found a strong dependence of the enhancement effects on the considered secondary ion species and a smaller averaged secondary ion emission depth for molecular primary ion bombardment. We will summarize our experimental results and will discuss them in the frame of a simple model. Whereas yield and damage cross section enhancements can be explained - at least partially - by an increase in sputter yields, the observed increase in ion formation efficiencies for molecular primary ions indicates a more efficient ionization process for polyatomic primary ion impact.

4:40pm **AS1-MoA9 Quantitative ToF-SIMS and XPS Studies of Surface Structures in Alkyl Side-Chain Polyetherurethanes***, **S.C. Porter**, D.G. Castner, B.D. Ratner,* University of Washington

Surface enrichment of polyether soft segment (SS) is typical in segmented polyetherurethanes (PEUs). The incorporation of surface active side-chains (SC) into the relatively polar hard segment (HS) block of the polymer significantly alters the surface structure. PEUs having various lengths and densities of alkyl SCs were synthesized. XPS analysis showed that PEUs with long SCs had high surface concentrations of hydrocarbon (HC) chains. Similarly, HS blocks were drawn toward, and concentrated just below, the HC rich surface. Positive ToF-SIMS spectra of these polymers contained fragments unique to both the HS and SS of the PEUs. Numerous HC fragments from the set, (@super+@C@sub x@H@sub 2x+1@ and @super +@C@sub x@H@sub 2x-1@; x @<=@ 7), could be indirectly associated with the length and/or density of alkyl SCs. Negative spectra contained fragments unique to individual SC species and HS fragments analogous to those found in the positive spectra. Ion ratios were used to determine the HS/SS (pos. spectra) and SC/HS (neg. spectra) surface concentration ratios. The HS/SS and SC/HS ratios increased with both side-chain length and density. Comparison of log(HS/SS) to actual concentration ratios obtained from XPS data, yielded linear correlations. The correlations improved as the sampling depth of the XPS experiments approached that of SIMS. The presence of isomeric HS fragment pairs in both positive and negative SIMS spectra provided an intrinsic reference for direct comparisons of the intensity of the positive HC fragments with a negative SC fragment. An analytical relation based on theoretical ion intensities was established for a series of PEUs having the same SC. Ion ratios from the positive spectra and a ratio from the negative spectra were shown to be directly proportional. The proportionality constant was solely a function of the ionization probabilities for the various ions utilized. HC fragments which did not contain contributions from either the HS or SS showed good correlations with the SC fragment intensity.

5:00pm **AS1-MoA10 Molecular Secondary Neutral Emission from Molecular Overlayers under SF@sub 5@@super +@-Bombardment***, **A. Schnieders**, M. Schröder, D. Stapel, H.F. Arlinghaus, A. Benninghoven,* Universität Münster, Germany

It is well known that TOF-SIMS and in favourable cases laser postionization of sputtered neutrals (Laser-SNMS) are powerful tools for the analysis of organic surface species. Many efforts have been made to enhance the sensitivity and the efficiency of these techniques. Especially the use of polyatomic primary ions for the analysis of molecular overlayers results in an enhanced secondary ion emission compared to the use of atomic primary ions. We have investigated the influence of polyatomic primary ions on the secondary neutral emission with the intention to improve our understanding of the processes of molecular sputtering and ion formation. We used a reflectron-type time-of-flight mass spectrometer equipped with an electron impact gas ion source for sputtering. As primary ion species we chose Ar@super +@, Xe@super +@, and SF@sub 5@@super +@. For postionization of sputtered neutral molecular species a subpicosecond excimer laser system operating at 248 nm was available. As model systems we used molecular layers of adenine and alanine prepared on liquid nitrogen cooled substrates (Si, Au, ...). They were produced by evaporation of the molecules from a Knudsen cell under UHV condition. During overlayer formation the flux of sputtered secondary neutrals and secondary ions was continuously monitored under static sputtering conditions. We determined the influence of the substrate and of the layer thickness on the secondary ion and neutral yields under bombardment with the different primary ions. We found that neutral as well as ion yields from a submonolayer coverage are higher than for a multilayer. The yield enhancement depends on the sputtering conditions. We also determined kinetic energy distributions and disappearance cross sections as a function of layer thickness. A detailed discussion with special emphasis on the sputter process - including results on the internal excitation of sputtered molecules - will be presented.

Applied Surface Science Division
Room 6A - Session AS2-MoA

Applied Surface Science for Microelectronics

Moderator: C. Magee, Evans East

2:00pm **AS2-MoA1 Determination by XPS of the Reactions Taking Place at the Semiconductor/'Heteropolyanion Solution' Interface***, A. Quennoy, A. Rothschild, A. Etcheberry,* CNRS - France*; **C. Debiemme-Chouvy**,* CNRS - France, FRANCE

When semiconductors (SC) are immersed in a solution containing oxydizing species they could undergo an oxidation/dissolution process. Therefore their surface chemical composition can evolve. The knowledge of the SC surface composition after the treatment allow sometimes to determine the reactions which had taken place at the SC/solution interface. In this communication, an example will be shown. The heteropolyanions (HPA) based on oxometallate compounds can undergo multiple one- or two-electron reduction of the metallic atoms. @footnote 1@ Thus depending on their oxidizing power they could oxidize SC. We studied the behavior in acidic solution of two HPA species with a Keggin structure H@sub 4@SiW@sub 12@O@sub 40@ (SiW@sub 12@) and H@sub 4@SiMo@sub 12@O@sub 40@ (SiMo@sub 12@) toward GaAs. The XPS analyses shown that after immersion in the HPA solution a deposit is formed on the GaAs surface. For immersion longer than one hour the substrate is no more detected. The deposit obtained in the presence of SiW@sub 12@ is composed of WO@sub 3@.@footnote 2@ Concerning SiMo@sub 12@, the HPA structure seems conserved in the deposit. Moreover the peak fitting of the Mo3p XPS spectrum indicates that some Mo atoms have remained at the oxidation state (VI) and that others have reached the oxidation state V. Otherwise, whatever the HPA studied As atoms are present in the deposit. They are at an oxidation state higher than that of As atoms inside the substrate. All these results indicate that in the presence of SiW@sub 12@ or SiMo@sub 12@ GaAs is oxidized while the HPA species are reduced. The conclusions obtained just on the basis of the XPS analyses were confirmed by electrochemical studies and profilometry. @FootnoteText@ @footnote 1@ M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, Heidelberg, 1983. @footnote 2@ A. Rothschild, C. Debiemme-Chouvy, A. Etcheberry, Applied Surface science 135 (1998) 65.

2:20pm **AS2-MoA2 Sputter Deposition and Annealing of Ta, TaSi and Ta@sub 4@B Composite Films and Their Application in Next Generation Lithography Masks***, **K. Racette**, C. Brooks,* IBM

Ta and Ta composites with other elements have been developed by several researchers as low stress absorbers for x-ray mask technology. These thin films are often produced in small quantities by sputter deposition from targets of pure Ta with chips of the minor elements placed on the target to create the composites. For membrane-mask manufacturing it is important that absorber films have uniform composition, thickness and low stress to assure that image size and pattern placement errors are minimal. Since sputter deposited films containing Ta have highly compressive stress, several methods have been used to reduce the final stress, including careful control of sputtering conditions, deposition of layered films with different stresses, and thermal annealing. Much data has been reported on the effects of thermal annealing of Ta films but less information is available on multiple element films such as TaSi and Ta@sub 4@B. Reports have generally been developmental in nature and not discussed behavior of these films under longer term, higher volume manufacturing conditions. During the last several years IBM has been engaged in development and fabrication of refractory x-ray membrane-masks using TaSi and Ta@sub 4@B as absorber materials. Films were sputter deposited from hot isostatically pressed powder targets of Ta, Si, and B using an S-gun cluster deposition system. This paper will report on the deposition and annealing of these films and their application to membrane-mask fabrication in a manufacturing environment. The effects of deposition parameters such as dc power, argon gas flow (pressure) and substrate on film stress, composition and density will be dicsussed. The results of air and nitrogen annealing on thick and thin films of TaSi and Ta@sub 4@B will be presented. Absorber film quality data and its impact on image size, pattern placement and defect density of some fabricated x-ray masks will be presented.

2:40pm **AS2-MoA3 XPS Sputter Depth Profiling at the Pd/Y Interface@footnote *@**, ***G. Neuert***, *R.J. Smith,* Montana State University*; J.A. Schaefer,* Technische Universität Ilmenau, Germany

X-ray photoelectron spectroscopy (XPS) sputter depth profiling, Rutherford Backscattering Spectroscopy (RBS) and in situ resistivity measurements are used to study the Pd-Y interface. This interface is of interest because of recent work showing that Pd-capped Y films exhibit a reversible metal semiconductor transition as a function of H content in the film. The yttrium film was first evaporated on a glass substrate. A palladium layer was then evaporated on the top of the yttrium film. Both films are made by thermal evaporation using a tungsten basket with a boron-nitride crucible as heating shield. RBS is used to measure the thickness of the film and to calibrate the sputter rate for pure Pd and Y. Palladium 3d photoelectron peaks, measured by XPS, show a core level shift to higher binding energies with sputter depth. This chemical shift can be an indication of alloy formation at the Pd / Y interface. The resistance measurements are done in situ by a four probe measurement after van der Pauw. The resistance of the yttrium film is measured after finishing the yttrium evaporation. A palladium layer was then evaporated on the top of the yttrium and the resistance of the films was monitored during Pd evaporation. @FootnoteText@ @footnote *@Work supported by NSF DMR 97-10092 and NASA EPSCoR NCCW-0058. Permanent address of G. Neuert : Institut für Physik, Technische Universität Ilmenau, P.O. Box 100565, D-98684 Ilmenau, Germany.

3:00pm **AS2-MoA4 Thin Film Characterization through combined X-ray Photoelectron Spectroscopy (XPS) and X-ray Diffraction (XRD)**, ***D.J. Surman***, *S. Bates,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Inc., UK*; J.E. Fulghum,* Kent State University

Traditionally there has been a range of methodologies applied to the analysis of thin films, centering on the use of XPS combined with sputter profiling. This approach provides both elemental and chemical information for each of the layers within the film. Following calibration with standard materials, a measure of the sputter rate can be obtained allowing allowing film thickness estimations to be made. It is well known however that different materials sputter at different rates and therefore it is difficult to obtain accurate measurements of individual layer thickness without extensive calibration. X-ray Diffraction (XRD) offers new possibilities for the characterization of thin films. Recently developed poly-capillary optics enable the generation of intense parallel beams of X-rays. This X-ray beam can then be used at grazing angles to provide a range of additional information on the nature of the thin film. This methodology allows accurate film thickness measurements to be obtained from monolayer to approximately 2000Å.This can be applied to multi-layer structures, providing an accurate measure of the individual layers enabling in-situ callibration of the sputter profile. The X-ray diffraction pattern also allows the polycrytalline phases within the film to be identified and quantified, providing additional support information for the chemical information provided by XPS. Variation of the diffraction pattern with grazing angle can also be used to obtain a measure of film thickness' of greater than 2000Å. This paper will demonstrate the enhanced characterization that can be achieved through the combined use and interpretation of the XPS and XRD data on a series of different materials and combined thin films.

3:20pm **AS2-MoA5 Photoelectron Spectroscopic Investigation of Interfaces and Thin Layers for Microelectronics: Composition and Chemistry as a Function of Depth**, ***R.L. Opila***, *J.P. Chang, J. Eng, Jr., M. Du,* Bell Labs, Lucent Technologies **INVITED**

As dimensions shrink in microelectronics, the role of interfaces between materials becomes more important and the characteristic dimensions of microelectronics approach the escape depth of photoelectrons. Two strategies to examine thin layers and their interfaces will be described. First, the overlayer will slowly be deposited, the specimen will be transferred in vacuo, after which the photoelectron spectrum is recorded. This strategy has proven to be particularly useful in determining how metals react with polymers, which are being considered as low dielectric constant interlayers between conductors. Because it is desirable to use copper despite its poor adhesion, barrier layers of more reactive metals and their nitrides must be incorporated. We have successfully used photoelectron spectroscopy to study the chemistry that occurs between a series of low dielectric constant materials, including fluoropolymers and aerogels, and titanium, tantalum and their nitrides. The relative reactivity at the interface controls the morphology of the growing overlayer. The interface between the barrier metal and the copper seed layer has been studied. In another application of photoelectron spectroscopy, the composition and chemistry of oxide layers for use as gates in transistors or as dielectrics in capacitors have been studied. The thickness of the dielectric layer is comparable to the escape depth of the photoelectrons. Thus, we have been able to identify certain chemical states as those likely to act as defects in the electronic device. Moreover, using angle resolved photoemission, the composition of the dielectric overlayer has been determined as a function of depth for silicon oxynitrides and tantalum pentoxide. A maximum entropy algorithm to transform the angle resolved data to elemental and chemical depth profiles will be described. Reactions that occur at the buried interfaces between the dielectic and the underlying electrode will also be described.

4:00pm **AS2-MoA7 Analytical Conditions for Semi-Quantitative Auger Analysis of TaN**, ***C.F.H. Gondran,*** SEMATECH*; D.C. Nelsen,* SEMATECH, on assignment from Intel*; D.A. Hess,* Evans Texas

Historically, quantitative analysis of tantalum nitride (TaN) has been done by Rutherford backscattering spectroscopy (RBS), to avoid problems due to preferential sputtering effects seen in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). Recently tantalum (Ta) and TaN have emerged as leading candidates for barrier layers in advanced metalization schemes for next generation semiconductor devices. The small size of the features in these devices, as small 0.25 micron and shrinking, necessitates the development of a procedure to perform at least semi-quantitative analysis of TaNx films by a technique with significantly higher spatial resolution than RBS. In this paper the preferential sputtering effects seen in TaN by AES and XPS are characterized as a function of ion beam energy and film composition. This data is used to determine the most favorable analytical conditions for semi-quantitative AES analysis and develop an understanding of the limitations.

4:20pm **AS2-MoA8 Investigation of InP(110) Surface Damage Induced by Low Energy Ar and He Ion Bombardment**, ***Q. Zhao***, The Chinese University of Hong Kong, P.R. China*; Z.W. Deng,* Tsinghua University, P.R. China*; R.W.M. Kwok, W.M. Lau,* The Chinese University of Hong Kong, P.R. China

High-resolution x-ray photoelectron spectroscopy (XPS) was employed to study the surface damage on n- and p-InP(110) caused by low energy ion bombardment in an ultrahigh-vacuum (UHV) system. The dynamic process of surface Fermi level shifting induced by ion bombardment as a function of ion dosage and ion energy was also measured. Two kinds of ion He@super +@ and Ar@super +@ at 10eV and 100eV energy with different ion dosages (from 10@super 12@ to 10@super 17@ ions/cm@super 2@) were chosen to investigate the performance of ion bombarded InP(110) surface. The results showed that the Fermi levels of both n- and p InP (110) surface moved to the midgap due to He@super +@ and Ar@super +@ ion bombardment, and ultimately pinned at about 0.95eV above the valence band maximum. More importantly, it was found that even at a bombardment energy of 10eV, ion fluence of 5x10@super 16@/cm@super 2@ was enough to cause an electrically active bandgap state density of 1x10@super 12@/cm@super 2@ which can detrimentally affect the device performance of the semiconductor.

4:40pm **AS2-MoA9 Phase Transformation of Cubic Boron Nitride Induced by Ion Bombardment**, ***B. Zheng***, The Chinese University of Hong Kong, P.R. China, Hong Kong, P.R. China*; R.W.M. Kwok,* The Chinese University of Hong Kong, P.R. China*; M.Y.Y. Hui,* The Chinese University of Hong Kong, P.R. China, Hong Kong, P.R. China*; W.M. Lau,* The Chinese University of Hong Kong, P.R. China

The effects of argon ion bombardment on cubic boron nitride in the energy range of 50-1000eV were studied by electron energy loss spectroscopy with a field emission scanning Auger microscope (PHI 670), and by Auger and photoelectron emission. The microanalysis capability of the microscope allowed data collection from a (111) facet of a cubic boron nitride crystal, which largely increased the accuracy in the determination of the ion bombardment effects. Through monitoring the conversion of the electron energy loss features of cubic boron nitride to those of hexagonal boron nitride with an incident electron beam energy of 250eV, we determined the cubic to hexagonal phase transformation as a function of ion fluence and ion energy with a sub-monolayer sensitivity. We found that even at the low end of our bombardment energy range, the cubic to hexagonal phase transformation was still evident.

5:00pm **AS2-MoA10 Guided Ion-beam Studies of Low Energy Cu@super +@ and Cu@sub 2@@super +@ Ion Interactions with Ni(100)**, *S.L. Anderson*, ***A. Lapicki***, *K.J. Boyd, M. Aizawa,* University of Utah

Low-energy (5-220 eV) Cu@super +@ and Cu@sub 2@@super +@ ions are deposited on Ni(100) under UHV conditions using the phase-space compressing ion beam deposition system at the University of Utah. The nature of the deposited Cu is determined by variable angle XPS and XAES. The disposition of the Cu deposits is explored as a function of ion energy and species. The Cu-Ni system exhibits stable surface and bulk alloys, and thus provides an interesting comparison to the C metal systems previously studied by ion beam methods (Ag/Ni, Cu/Mo). The influence of system thermodynamics and ion energy effects are examined via experiments and computer simulations.

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI+VM+AS-MoA

Magnetic Recording: Media and Heads

Moderator: D.E. Fowler, Maxtor Corporation

2:00pm **MI+VM+AS-MoA1 Spectro-Microscopy of Magnetic Materials Using Polarized Soft X-Rays***, **J. Stohr**,* IBM Almaden Research Center **INVITED**

The talk discusses the motivation for and challenges of obtaining magnetic information for ferromagnetic and antiferromagnetic systems on a length scale below 100nm. It reviews the principles of linear and circular x-ray magnetic dichroism spectro-microscopy and presents state-of-the-art results (20nm resolution) obtained with a dedicated soft x-ray photoelectron emission microscope (PEEM) installed on the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Results include studies of the antiferromagnetic domain structure at the surface of LaFeO3(100), NiO(100) and polycrystalline NiO and the ferromagnetic domain structure in hard/soft magnetic tunnel junctions. Future plans to reach a spatial resolution below 10nm will also be discussed.

2:40pm **MI+VM+AS-MoA3 Micromagnetic Properties and Recording Performance in High Density Magnetic Recording Media***, **T. Suzuki**, G. Lauhoff,* Toyota Technological Institute, Japan **INVITED**

In order to increase areal recording density, much effort has been made to improve magnetic charactreristics and microstructure in magnetic recording media. In order for decreasing noise and for realizing a sharp transition between written bits, an inter-granular exchange coupling must be lowered, which enhances a thermal instability of magnetization. Given this conditions, it is vitally important to understand the role of magnetic activation volume or magnetic coupled region in conjunction with micromagnetics, which plays a key role in noise mechanisms. The present study is to discuss activation volume in longitudinal magnetic recording media of various types including CoCrPtTa thin-films and granular-type recording media. The activation volume is evaluated based on the time decay of magnetization at a certain field. A novel method to define the activation volume is proposed. The Barkhausen volume is estimated through the field-sweep-rate dependence of coercivity. It is found that the activation volume, which is of the order of 10@super -18@ cm@super -3@, decreases with applied field, then levels off, and starts increases at fields beyond coercivity. This trend is found for all the high density recording media of CoCrPtTa and granular-type media under consideration. The recording noise is found to be closely related to activation volume. Measurments of @delta@M curves suggest that lesser the granular-exchange-coupling is, the smaller the activation volume becomes.

3:20pm **MI+VM+AS-MoA5 Sub 50 nm Planar Magnetic Nanostructures Fabricated by Ion Irradiation***, T. Devolder, **C. Chappert**,* IEF/Université Paris Sud, France*; Y. Chen,* L2M Bagneux/CNRS, France*; H. Bernas,* CSNSM/Université Paris Sud, France*; J.-P. Jamet, J. Ferré,* LPS/Université Paris Sud, France*; E. Cambril,* L2M Bagneux/CNRS, France **INVITED**

Areal density enhancement is a major challenge in magnetic recording. Near field magneto-optical techniques are one fast-developing attempt to respond. At bit density values above 65 Gbits/in@super 2@, a most drastic requirement will be to write stable bits with nanometer wall jaggedness, at very precise locations on the disk. Patterned media could be a promising response to this problem.@footnote 1@ However, surface roughness, and polarization dependent effects due to abrupt changes in optical index, will likely deteriorate the signal to noise ratio. Through interface mixing, light ion (He+) irradiation can modify in a precisely controlled way the magnetic properties of multilayers, with negligible change of surface roughness and optical indices. In (Co/Pt) multilayers with perpendicular easy magnetization axis, the anisotropy decreases with irradiation, which first reduces the coercive force, then induces in-plane magnetization. Patterning only the magnetic properties can then be obtained by irradiation through a lithographic PMMA resist mask.@footnote 2@ Using SiO@sub 2@ masks, we have fabricated regular arrays of such irradiation-patterned nanostructures with sizes down to 30 nm. Different configurations such as hard (resp. soft) nanostructures in soft (resp. hard) media have been obtained and characterized using far field magneto-optical microscopy. Special attention has been devoted to the study of the transition zone between irradiated and protected areas, and its effect on magnetization reversal. The technique may be a powerful tool for ultrahigh density magnetic recording applications. @FootnoteText@ @footnote 1@ S. Chou et al., Data Storage 35 (1995). @footnote 2@ C.Chappert et al., Science 280, 1919 (1998).

4:00pm **MI+VM+AS-MoA7 Crystallographic Texture and Stress in Co-Based Magnetic Recording Media and Underlayers***, **B.M. Clemens**, G. Khanna,* Stanford University **INVITED**

The magnetic and recording properties of Co-based media are a strong function of crystallographic texture and stress in the media layers, which are in turn strongly influenced by the texture and stress of the Cr underlayer. The anisotropy in strain and the distribution of c-axes in the hcp Co alloy media can determine the magnetic hysteresis anisotropy through magnetostrictive and magnetocrystalline effects. The processing conditions and mechanical texture grooves in the NiP/Al substrate strongly influence the microstructural and mechanical properties of the Cr and Co films. We report x-ray studies of the texture and strain in Cr and Co-based films sputter deposited over a range of temperatures and substrate biases on smooth and mechanically textured substrates. All films showed an in-plane compressive stress. The magnitude of the stress in Cr and Co films grown without a substrate bias decreases with decreasing growth temperature, consistent with thermal mismatch stress. The stress in the Cr films grown with a -300V bias was greater than that of unbiased films, and independent of growth temperature. This suggests that the bias-induced stress is close to the yield stress of the film. However, the biased Co films show a decrease in compressive stress with decreasing temperature. For mechanically textured substrates, the stress measured in the direction perpendicular to the texture grooves was less compressive relative to the parallel direction in both Cr and Co. However, the stress anisotropy vanishes in smooth substrates. A simple strain relaxation model is used to explain the observed Cr stress values in the textured disks. The anisotropic strain in the Cr may also account for the observed preferential alignment of Co c-axes along the grooves. Calculation of the magnetoelastic and magnetocrystalline energies predicts that Co stress anisotropy and the preferential alignment of Co c-axes along the grooves both contribute to the observed hysteresis anisotropy.

4:40pm **MI+VM+AS-MoA9 Noise in GMR Recording Heads***, **H.T. Hardner**, M.B. Hurben,* Seagate Technology **INVITED**

Magnetoresistive sensors exploit a close coupling between magnetization and resistance to convert changes in magnetic field to an electrical signal. Thus, the enhanced sensitivity of the giant magnetoresistive (GMR) materials to magnetic field is accompanied by larger electrical noise due to magnetization noise. A magnetic contribution to 1/f noise originates in thermal fluctuations in magnetization. This is a concern for sensors intended for low frequency applications rather than for magnetic recording heads due to the very high frequencies at which the heads operate. However, discrete steps in the resistance can also appear due to large discrete changes in domain structure. When these steps occur as a continuous magnetic signal is applied to the device they are called Barkhausen noise. In small enough devices discrete magnetoresistive steps can be observed even at fixed magnetic field. While the sensitivity of the resistance to changes in magnetization is proportional to the magnetoresistance, the propensity for complex domain structure with fluctuations between multiple metastable states varies by material, processing, and design. The suppression of these fluctuations to create a device with a single stable magnetization state is a key goal in the design and manufacture of magnetoresistive recording heads. This talk will provide some brief background on how recording heads are stabilized as well as an overview of resistance noise data from GMR devices including comparisons of different materials and the use of resistance noise measurements to study domain structure. Recent results on resistance noise in spin-valve recording heads both at the finished stage and during wafer processing will be presented along with discussion of how a detailed study of electrical noise can help identify stability problems. Analysis of both time and frequency domain data will be considered.

Tuesday Morning, October 26, 1999

Applied Surface Science Division
Room 6A - Session AS-TuM

Ion Beam Analysis and Depth Profiling

Moderator: F.A. Stevie, Lucent Technologies

8:20am **AS-TuM1 Characterization of Shallow Junctions Using Secondary Ion Mass Spectrometry**, ***C. Magee**, I.M. Abdelrehim, T.H. Buyuklimanli, J.T. Marino, W. Ou,* Evans East **INVITED**

As design rules drop below 0.25um, there is a need for developing methodologies to form ultra-shallow junctions for the source and drain extension areas of FETs. Ultra-low energy ion implantation and plasma doping appear to be the leading candidates to form these junctions. However, these techniques need to be followed by some kind of annealing step to activate the dopant. This talk will show how SIMS can be used to characterize the as-implanted distributions for ultra-low energy implants of B, P and As, as well to characterize the degree of dopant diffusion that occurs during annealing. This will be prefaced by a discussion of the problems inherent in SIMS analysis of such shallow structures. These problems arise from atomic mixing from the primary ion beam and surface roughening during the analyses.

9:00am **AS-TuM3 Quantitative Determination of Oxide Layer Thickness and Nitrogen Profiles for Si Gate Oxides**, ***O. Brox**,* Universität Münster, Germany; *K. Iltgen,* AMD Saxony Manufacturing GmbH, Germany; *E. Niehuis,* ION-TOF GmbH, Germany; *A. Benninghoven,* Universität Münster, Germany

Accurate characterization of ultra-thin nitrided gate oxides is crucial for future semiconductor device scaling. We have investigated the capabilities of TOF-SIMS to control oxide thicknesses down to 2-3 nm and to quantify the nitrogen depth distribution. For all experiments we used the TOF III instrument, equipped with a flexible gas ion source and a cesium source (0.6 - 10 keV) for crater formation. An additional gas ion source (Ar@super@+, 11 keV) was applied for the analysis of the crater bottom. SiO@sub 2@ layer thicknesses can be determined by measuring exactly the position of the SiO@sub 2@/Si interface during depth profiling. This interface is indicated by drastic changes in the yield of the characteristic secondary ion species Si@sub x@O@sub y@@super -@. We found that the maximum in the Si- emission describes the position of the SiO@sub 2@/Si interface very exactly and that down to less than 3 nm oxide thickness a linear relationship exists between the position of this maximum and the oxide thickness as determined by TEM. We determined the nitrogen concentration in the oxide layers by following the nitrogen specific secondary ion SiN@super -@ and at the same time the SiO@sub n@@super -@ (n=0,1,2,3) intensities, which allow to calculate the corresponding lattice valency [1]. Relative sensitivity factors for nitrogen as a function of lattice valence were determined by using a nitrogen implant sample with a known nitrogen concentration. This allows to correct the measured SiN@super -@ profiles. We will report on these depth profiling results, the strong influence of the sputter ion energy on the width of the transient regime, changing between 1 nm for 0.4 keV and about 8 nm for 5 keV, on the influence of sample temperature during sputtering and on possible improvements by applying sputter ion energies @<=@ 0.4 keV combined with simultaneous Cs and noble gas sputtering. . @FootnoteText@ [1] C. Plog, L. Wiedmann, A. Benninghoven, Surf. Sci. 67 (1977) 565.

9:20am **AS-TuM4 Cesium Depth Profiling of Ultra-Shallow Implants**, ***E. Niehuis**, T. Grehl, D. Lipinsky,* ION-TOF GmbH, Germany; *O. Brox, A. Benninghoven,* Universität Münster, Germany

Currently fabricated junction depths are between 50 nm and 100 nm, and they will decrease to about 10 nm for future deep sub-micron process technology. High depth resolution SIMS profiling is needed to control implant dose, junction depth, dopant distribution and its modification by thermal and chemical processes. In order to improve the depth resolution of SIMS, primary beam energies have been reduced over the last few years from several keV to a few hundred eV. In particular, oxygen depth profiling of B in Si in the sub-keV range has been studied in great detail over the last 2 years. In Cs depth profiling at low energies for the analysis of electronegative elements like As and P in Si two specific problems arise: 1. The decrease of the sputter yield with Cs energy results in a significant increase of the Cs surface concentration under steady state conditions. This has a strong influence on secondary ion emission and results in erosion rate changes in the transient regime. 2. A significant part of the implant dose is located in a native oxide or a screening oxide of the implantation process. Negative SI yields in a SiO@sub 2@ and Si matrix are quite different leading to errors in profile shape and implantation dose. We have investigated Cs sputtering at sub-keV energies using a TOF-SIMS instrument in the dual beam mode. A low energy Cs beam generates the sputter crater while a pulsed Ga beam at 15 keV energy probes the composition in the center of the crater. As the conditions of the analytical beam (energy, angle, spot size) are not changed with Cs beam energy, this dual beam mode is well suited for systematic studies in the very low energy regime. This paper will discuss the change of the positive and negative SI emission and erosion rate for SiO@sub 2@ and Si with Cs sputter energy. In addition, we investigate correction procedures in the transient regime and at the SiO@sub 2@/Si interface region.

9:40am **AS-TuM5 Characterization of Ultra-thin (2-3nm) Oxide Films using Low Energy Cs Ion Beams**, ***D.F. Reich**, B.W. Schueler,* Physical Electronics; *J. Bennett,* Sematech, U.S.A

The thickness of silicon dioxide used as the transistor gate dielectric in most advanced memory and logic applications has decreased below 7nm, and is predicted to fall to 2-3nm for the next generation of devices. Characterization of thin oxide and nitrided oxide films by SIMS is currently achieved in quadrupole mass spectrometers using low energy primary Cs+ ions (0.75-2keV) at an angle of incidence of 60 degrees. Under these conditions, the preferred analysis method is to use MCs+ secondary ion monitoring in +SIMS, as this results in reduced matrix effects. For SIMS analysis of 2-3nm films, it is desirable to reduce the primary beam energy below 750eV, since the decay length and depth resolution even at this energy are comparable to the film thickness. Unlike the CsM+ results obtained with 0.75-2keV Cs+ beams at 60 degrees incidence, results with @<=@ 500eV Cs+ at angles from 60-75 degrees show matrix CsSi+ signals that are not in equilibrium in the near surface of the silicon substrate. By contrast, a 500eV Cs+ beam does result in constant matrix signals within the substrate when using ?SIMS. Interpretation of signals such as SiN- are, however, complicated by matrix effects at the oxide / silicon interface. The quadrupole SIMS instrument we are using employs ion columns with floating extractors. For the Cs column this results in useful primary beam currents of approximately 60nA at 500eV, and approximately 30nA at 250eV. Optimized off-axis extraction is possible using a split extractor when tilting the sample to vary the impact angle. To understand the CsM+ matrix signal variations at low primary energies, we report on measurements at Cs primary beam energies from 250-750eV, and at incidence angles of 60 and higher. Both +SIMS and -SIMS protocols are explored to understand optimum analytical conditions for characterization and quantification of 2-3nm ultra-thin oxides and oxynitrides.

10:00am **AS-TuM6 SIMS and XPS Correlation Study of Nitrided Gate Oxide**, ***C.A, Bradbury**,* Micron Technology Inc., US; *C. Blackmer,* Micron Technology Inc.

Reliability of dielectric films such as silicon dioxide in the gate has become a key issue as MOS devices shrink in size. Many of the problems associated with reduction in both the width and thickness of the gate oxide can be controlled with the addition of nitrogen. Nitrogen incorporation into the oxide has been shown to have significantly better charge trapping properties, less interface state generation, and more resistance to continued oxidation and incorporation of impurities. The nitrogen also acts as a barrier to diffusion of dopants from the silicon substrate. The amount of nitrogen present and its location in the oxide control the extent to which each of these properties is exhibited. The concentration and distribution of nitrogen in gate oxides was studied using Secondary Ion Mass Spectroscopy (SIMS) and X-ray Photoelectron Spectroscopy (XPS). The SIMS analysis used Cs ion bombardment and detection of the CsN+ cluster to reduce the matrix effects associated with profiling from silicon oxide into silicon. A procedure was developed for XPS to provide the necessary signal to noise required for these low nitrogen concentrations. In addition to comparing the concentrations and spatial resolution of the nitrogen in the gate oxide, repeatability studies were also performed for each technique.

10:20am **AS-TuM7 Characterization of the Diffusion Properties of Metallic Elements Implanted into Silicon by SIMS**, ***H. Francois-Saint-Cyr**, E. Anoshkina,* University of Central Florida; *F.A. Stevie,* Cirent Semiconductor/Lucent Technologies; *L. Chow, K. Richardson, D. Zhou,* University of Central Florida

Metallic elements introduced during device processing degradation or failure of semiconductor devices. Therefore, a better understanding of diffuison phenomena of metallic elements in silicon is useful for quality control and failure analysis. However, the diffusion data of many elements implanted into silicon are not readily available. Because of high sensitivity and excellent depth resolution, secondary ion mass spectrometry (SIMS) is the dominant analytical technique for determining the impurity profiles. When ion implantation, post-heat treatment, and SIMS analysis are combined, the diffusion characteristics of selected metallic elements can be better understood. A systematic investigation of the diffusion of Mg, Cl, K, Ge, Mo, Ca, Ti, V, Cr, and Mn has been carried out employing SIMS. These elements have been initially implanted into silicon wafers as low dose impurities, and then post-heat treatments of the ion-implanted samples have been conducted at different temperatures for a specific time. Following the post-annealing treatments, the depth-profiles of those elements have been obtained by the SIMS analyses. A wide range of diffusion behaviors has been observed for these elements. There possible, quantification of the diffusion process has been achieved based on the differences of the depth-profiles. Furthermore, the diffusion phenomena of different elements are discussed in terms of the activation energy, electronic structures and radii of ions, and their diffusion coefficients.

10:40am **AS-TuM8 Focused Ion Beam Micromachining of Thin Film Copper***, **J. Phillips**, D. Griffis, P.E. Russell,* North Carolina State University

The focused ion beam (FIB) sputtering behavior of thin film copper has been investigated as a function of tilt and rotation of the sample with respect to the incident ion beam. Thin film and single crystal copper was used for this study. The thin film samples were deposited by vapor deposition and shown by x-ray diffraction to be textured . A significant sputter rate increase was observed when milling textured copper at 12 degrees tilt, regardless of sample rotation. In an effort to understand the origin of this sputter rate enhancement, the orientation dependence of single crystal copper (111) was examined. Rotating the sample about [111] with various tilt increments (0-28 degrees in 4 degree steps) demonstrated that channeling effects were responsible for the increased sputter rate, as has been observed.@footnote 1@ In an effort to correlate the single crystal results with the thin film observations, (111) single crystal data was averaged over all rotations to give an overall material removal rate for each sample tilt. Data averaged in this manner directly correlates, within experimental error, with the thin film data suggesting that the crystallinity of the thin film copper is responsible for the observed sputter rate variation. Thus the FIB material removal rate of copper films can be increased by up to 30% by tilting the sample 12 degrees with respect to the ion beam axis. @FootnoteText@ @footnote 1@R. Behrisch, Sputtering by Particle Bombardment I, Springer-Verlag, New York, 1981, pp. 260, 300, 301.

11:00am **AS-TuM9 Surface Analysis and Depth Profiles of Self-healing Copper Aluminum Alloys********, **J.F. Moore**, W.S. Calaway, I.V. Veryovkin, M.J. Pellin,* Argonne National Laboratory

An investigation of the self-protecting properties of Cu@sub 3+x@Al@sub 1-x@ with ternary components (including small amounts of Ag, Ni, Mg, and Mn) is presented. When these alloys are heat treated, a self-terminated (micron-scale) layer rich in alumina is typically formed. The surface film, in principle, can protect the bulk alloy from chemical attack, for example in a molten salt, while maintaining desirable properties of conductivity and thermal stability. In this way the bulk and surface properties of the alloy may be separately optimized. Further, under these circumstances the film can regenerate if dissolved or damaged by rapid diffusion and oxidation of aluminum at the surface. To understand the properties of the initial thermal oxide, we have undertaken surface and depth profiling studies of these alloys using Auger and x-ray photoelectron spectroscopy and secondary neutral mass spectrometry. Results show a strong dependence of the surface composition with heat treatment temperature, alloy composition and oxygen environment. Depth profiling indicates a mixed, aluminum-rich oxide with long diffusion lengths for components in the bulk metal. @FootnoteText@ *Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-ENG-38.

11:20am **AS-TuM10 Quasi Atomistic Depth Resolution with Auger Depth Profiling for Oxide / Metal Structure***, **M. Menyhard**, A. Barna, Zs. Benedek, A. Sulyok,* Research Institute for Technical Physics and Materials Science, Hungary

By applying specimen rotation, and grazing angle of incidence for depth profiling, the depth resolution is limited by atomic mixing. To achieve depth resolution of less than 1 nm we have two possibilities; either to decrease the ion energy or to find evaluation routine to correct the effect of atomic mixing. Using very low ion energy, however, the sputtering rate is small resulting in practical problems e.g. extreme cleanliness long measuring time is necessary. Thus it is of great importance to develope evaluation routines for the correction of atomic mixing. We have shown that our trial-and-error routine based on dynamic TRIM simulation can be successfully applied@footnote 1,2@ for the evaluation of the depth profiles where the layers are made of elements with no affinity for compound formation. In this contribution we will report on the extension of our evaluation method for the case of oxide / metal structure. Well characterized silicon oxide /silicon, and oxynitride / silicon structures (specimens were kindly provided by E. Garfunkel of U. Rutgers) with various thickness were depth profiled applying various sputtering conditions. At 0.4 keV Ar sputtering (where the measurement time is reasonable) the depth resolution was found to be around 0.7 nm, while at 0.2 keV better than 0.4 nm. At this later energy, however, practical studies cannot be performed because of the long measuring time. Our evaluation routine was parametrized to reproduce the experimentally measured depth profiles for a given sputtering condition. It turned out that using the same parameters the simulated and measured depth profiles agreed well for the various sputtering conditions. In this way we can apply the higher ion energy (0.4 keV) for routine analysis and using the evaluation routine depth resolution about 0.4 nm could be obtained. @FootnoteText@ @footnote 1@M. Menyhard, Surf. Interface Anal. 26 1001 (1998). @footnote 2@M. Menyhard and A. Sulyok, J. Vac. Sci.Tech A16 1091 (1998).

Magnetic Interfaces and Nanostructures Technical Group
Room 618/619 - Session MI+VM+AS-TuM

Magnetic Recording: Media

Moderator: H.T. Hardner, Seagate Technology

8:20am **MI+VM+AS-TuM1 Perpendicular Patterned Media: Fabrication and Demonstration of Data Storage***, **J. Wong**[1], A. Scherer,* California Institute of Technology*; M. Todorovic, S. Schultz,* University of California, San Diego

Patterned media has been proposed as one of the solutions to extending data storage densities beyond 100Gbits/in@super 2@. We have fabricated perpendicular patterned media using a combination of high resolution electron beam lithography, dry etching, and electroplating. Futhermore, we have successfully demonstrated data storage in such structures. We first use vector scanned electron beam lithography to define the dot array pattern on the PMMA coated Al@sub 0.9@Ga@sub 0.1@As/GaAs substrate. After development, this pattern is transferred into the substrate using Chemically Assisted Ion Beam Etching (CAIBE). Immediately following CAIBE, we convert the Al@sub 0.9@Ga@sub 0.1@As layer into (Al@sub 0.9@Ga@sub 0.1@)@sub 2@O@sub 3@ using wet thermal oxidation. We take advantage of the highly selective etching properties of GaAs and the durable masking properties of (Al@sub 0.9@Ga@sub 0.1@)@sub 2@O@sub 3@ to create high aspect ratio Ni columns. After the dot arrays are defined in the substrate, we use electroplating to fill the etched holes with Ni, followed by polishing.@footnote 1@ Using Magnetic Force Microscopy, we find that the Ni columns are stable single domain magnets. We demonstrate data storage in these structures by controllably orienting the magnetization of individual 170nm diameter Ni columns using conventional thin film write poles. We subsequently read back the stored information using current MR or GMR read heads.@footnote 2@ This demonstration bridges the gap between the fabrication of such structures and their use in actual magnetic storage systems. Work is in progress to characterize higher density arrays (~1.3, 2.6, and 5.2Gbits/in@super 2@) in the form of data tracks (1µm in the x-direction and 0.5, 0.25, and 0.125µm apart respectively in the y-direction). @FootnoteText@ @footnote 1@ J. Wong et al., J. Appl. Phys. 85, 5489, 1999. @footnote 2@ M. Todorovic et al., Appl. Phys. Lett. 74, 2516, 1999.

8:40am **MI+VM+AS-TuM2 Ion Beam Patterning of Magnetic Recording Media With a Stencil Mask***, **B.D. Terris**, L. Folks, D. Weller, J.E.E. Baglin, A.J. Kellock,* IBM Almaden Research Center*; H. Rothuizen,* IBM Zurich Research Lab*; P. Vettiger,* IBM Zurich Research Lab, Switzerland

In conventional scaling of magnetic recording media, the grain size is reduced as the bit density is increased, while the number of grains per bit is held approximately constant to maintain signal to noise levels. This scaling approach, however, will reach a fundamental limit when the grain sizes become so small that they are subject to reversal due to thermal excitation on time scales of less than the required data retention time. One approach to circumventing this thermal limit is to create magnetic bits that behave as single magnetic entities, e.g. either single domains or a collection of strongly coupled grains, rather than the hundreds of weakly coupled grains per bit found in conventional granular recording media. In one approach to

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[1] **Falicov Student Award Finalist**

patterned media, ion beam irradiation is used to locally alter the magnetic properties of thin Co/Pt multilayer films.@footnote 1@ With sufficient ion dose, the easy axis of magnetization is rotated from out-of-plane to in-plane. We have used this process in conjunction with a silicon stencil mask having 1 micrometer diameter holes to pattern regularly spaced micrometer-sized regions of magnetically altered material over areas of a square millimeter. The nature of these magnetic structures has been investigated by magnetic force microscopy. The technique is demonstrated with mask-sample spacing as large as 0.5 mm. In addition, smaller regions of magnetic contrast, down to 100 nm, were created by using two masks with partially overlapping micrometer holes. Unlike other patterning techniques, this approach is non-contact and does not require post-processing to clean the disk, both potential manufacturing advantages. @FootnoteText@ @footnote 1@ C. Chappert et al., Science 280,1919(1998).

9:00am **MI+VM+AS-TuM3 Ion Induced Magnetization Reorientation in Co/Pt Multilayers for Patterned Media***, **D. Weller**, J.E.E. Baglin, K.A. Hannibal, M.F. Toney, L. Folks, A.J. Kellock, M.E. Best, B.D. Terris,* IBM Almaden Research Center

Ion beam patterning of magnetic thin films using stencil masks is a prospective path towards ultrahigh-density magnetic recording media. Co/Pt multilayers are ideally suited for this application, since they undergo a spin-reorientation transition from easy axis out-of-plane to easy axis in-plane upon irradiation with ions of suitable energy and dose.@footnote 1@ The mechanism, leading to the observed modulation in magnetic properties is of great fundamental and technological interest and will be discussed in this paper. Electron beam deposited Co/Pt multilayers with representative structure [Si-substrate/SiNx/20 nm Pt buffer/10x(0.3nm Co/1 nm Pt)/2 nm Pt cap layer] were used. These structures have high coercivity (H@sub C@ = 5000- 8500 Oe) and exhibit square perpendicular hysteresis. The high coercivity is attributed to the the large perpendicular anisotropy (K@sub u@ = 4.3 10@super 7@ erg/cm@super 3@) and granularity of these films as indicated in AFM surface topography measurements. The structures were subjected to various doses and currents of 700 keV N@super +@ ions and investigated after each irradiation step using grazing incidence X-ray reflectivity and Kerr hysteresis loop measurements. Direct evidence for ion beam mixing at the Co/Pt interface is found from the XRD data. In particular, we find an almost linear decrease of the integrated intensity of the first grazing incidence Bragg peak with ion dose. This correlates with the measured remanence ratio and anisotropy, however, not with the coercivity, which drops off much faster. @FootnoteText@ @footnote 1@ C. Chappert et al., Science 280, 1919 (1998).

9:20am **MI+VM+AS-TuM4 Texture and Strain in Cr/NiAl Films Grown on Glass Substrates***, **G. Khanna**[1], B.M. Clemens,* Stanford University

Glass has recently emerged as a promising candidate to replace NiP/Al in magnetic recording media due to its smooth surface and high shock resistance. A NiAl seed layer may be employed to produce the desired (112) orientation in the Cr underlayer and a (1010) orientation in the Co-alloy magnetic layer. Since NiAl forms the template for subsequent growth of Cr and Co, determining its growth texture and strain is critical to understanding the microstructure and magnetic properties of the media. We report on synchrotron radiation experiments on Cr/NiAl films of various thicknesses grown on glass substrates at elevated temperatures. Our results demonstrate that the growth of the NiAl (and consequently the Cr) on glass substrates is markedly different from Cr growth on traditional Al/NiP substrates. While a strong (002) out-of-plane texture develops at elevated temperatures in the latter case, no particular growth orientation dominates in the NiAl. Both (110) and (112) reflections appear out-of-plane in Cr films grown on thin seed layers. This result indicates that both growth orientations are present in the NiAl since the Cr grows epitaxially on the NiAl surface. Furthermore, several out-of-plane reflections appear in thick NiAl films which implies that, initially, there is simultaneous growth of NiAl grains having several different orientations. Integrated intensities of (110) reflections suggest that NiAl (110) grains are overgrown as the film thickness increases. A comparison of pole figures shows that the NiAl (110) peak is shifted to @Delta@ @psi@ = 30 from the out-of-plane direction for thicker films. The evolution of the texture with depth may be quantified using grazing incidence geometry and varying the incident angle. Intensity ratios from GIXS in-plane reflections corresponding to particular out-of-plane orientations are used to depth profile the texture. The in-plane reflections may also be used to determine the inhomogeneous strain in both layers.

9:40am **MI+VM+AS-TuM5 Ultrafast Magnetization Dynamics in Magnetic Thin Films***, **T.M. Crawford**,* Seagate Research **INVITED**

If one extrapolates the current growth trends for disc drive data rates, the data rate expected by the year 2005 is 2.4 Gbits/sec, requiring magnetization reversal frequencies in the GHz range. However, Permalloy (NiFe), a standard material used for inductive write heads, exhibits ferromagnetic resonance (FMR) at ~ 630 MHz, which is a 10%-90%, precession-limited switching time of 550 ps. While increasing the saturation magnetization and/or anisotropy shifts this resonance to higher frequencies, the gain in switching speed is proportional to only the square root of such increases. As a result, operating magnetic recording heads at or near the FMR frequency may be a necessity to achieve the desired data rates in future storage devices. This rapid increase in data rate toward the fundamental switching speed limit has generated renewed interest in the field of high speed magnetic switching and magnetodynamics, originally studied extensively in the 1950's and 1960's. This renewal has been assisted by the availability of faster electronic and optical techniques with improved signal-to-noise for characterizing magnetic materials and devices at times well below 1 ns. Recent contributions to this field in the form of time-domain switching measurements, where the film magnetization is driven far from equilibrium, will be reviewed. Subtle material-dependent phenomena which have been observed by these techniques, including possible differences in bulk and surface magnetic properties, will be discussed, as will the possibility of actively controlling the magnetodynamics to achieve a desired behavior. Finally, the extension of these techniques to more complicated materials systems and nanoscale device structures will be addressed.

10:20am **MI+VM+AS-TuM7 Temperature Dependent Characterization of Thermal Stability of Longitudinal Magnetic Recording Media***, **A. Moser**, D. Weller, E. Fullerton, K. Takano,* IBM Almaden Research Center

Temperature dependent characterization of thermal stability was performed on a series of magnetic recording media at temperatures between 300 K and 420 K using a static write/read tester.@footnote 1@ The investigated samples are CoPtCr alloys with thicknesses in the range between 5.5 nm to 13 nm. First, the thermal stability of a recorded bit track was studied by measuring the time-dependence of the read-back amplitude between 0.8 s and 70000 s. Second, the time-dependent coercivity was measured by applying a magnetic field pulse of 5 ns to > 60 s width opposite to the sample's initial magnetization. Finally, the samples were characterized by SQUID magnetometry yielding temperature dependent coercivities, viscosity parameters and irreversible susceptibilities. The measurements are discussed with a quasi-independent particle model. The measured stability ratios (ratio between energy barrier for magnetization reversal to thermal energy) and signal decay rates are found to decrease faster than simple scaling with temperature would predict. @FootnoteText@ @footnote 1@ A. Moser, D. Weller and M.E. Best, J. Appl. Phys. 85, 5018 (1999)

10:40am **MI+VM+AS-TuM8 High Resolution FE-Auger Electron Spectroscopy: Applications in Magnetic Recording, Heads and Media***, **C.A. Fenno**,* Seagate Technology - Colorado Design Center

As the Disk Drive Industry pushes toward higher capacity, smaller form factors, and better performance, head and disc design has changed considerably. Technological advances have resulted in decreased dimensions; thinner layers on the disc and within the head reader element, and lower flight heights. As a result the tools used in material characterization requires improved spatial resolution, increased depth resolution and increased spectral resolution. One answer to the challenge of evaluation and characterization of smaller disc and head features is FE-Auger Electron Spectroscopy. FE-Auger provides elemental analysis with excellent spatial resolution. In the best case the electron spot size can achieve 20nm although in the practical case on disc and head features an electron spot size of 60-100nm is more typical. Features of sub-micron dimensions are routinely analyzed with FE-Auger. In some cases high spectral resolution FE-Auger data can reveal chemistry as in the case of titanium-, silicon-, and aluminum-based particles as well as in the case of some oxides and carbides. This chemical data is obtained from particular energy shifts or peak shape change from the respective materials. This presentation will show several examples where the high spatial and spectral resolution available with FE-Auger was instrumental in diagnoses in drive failure analysis.

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[1] **Falicov Student Award Finalist**

11:00am **MI+VM+AS-TuM9 Characterization of Co/CN@sub x@ Granular Media Prepared by Nanolamination***, C. Ruby, J. Du, R. Zhou,* ***S.C. Street****, J. Barnard,* The University of Alabama

Cobalt-carbon thin films proposed for use as granular magnetic media are generally prepared by co-deposition sputtering. An alternative method is nanolamination of the component layers (media and matrix) followed by annealing. The potential advantages of this approach include precise control over component volume fractions and ease in fabricating large, uniform samples. We have produced and characterized thin film granular structures prepared from nanolaminate layers of Co and CN@sub x@. TEM studies of the microstructure indicate that for certain samples discrete domains are generated, with mean grain sizes of around 20 nm, with near lognormal distribution. These films have coercivities above 1200 Oe. Surface characterization by XPS depth profiling indicates that the annealed films have oxidized cobalt in the very near surface region, although initial study did not show any magnetic hysterisis loop shift. AFM measurements show that the surface of the film roughens significantly upon annealing, with the RMS roughness increasing from 0.2 nm to 1.0 nm. Thus, it appears that the mixing involved in the annealing process, which gives rise to grain formation, also degrades the smooth surface of the CN@sub x@ capping layer and exposes some of the cobalt to ambient. The implications of this process on tribological issues is explored.

11:20am **MI+VM+AS-TuM10 Characterization of Hard Disk Drives by Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)***,* ***B. Hagenhoff****, R. Kersting,* TASCON GmbH, Germany*; D. Rading, S. Kayser, E. Niehuis,* ION-TOF GmbH, Germany

Hard disks used in hard disk drives consist of a complex inorganic and organic layer structure. Whereas substrate near layers are inorganic of origin and can be comparatively thick, layers closer to the surface become very thin and are finally covered by an organic F containing lubricant. Defective production processes as well as normal use can change the original layer structure and composition. For an analytical characterization of these changes a technique is required which gives detailed information on the chemical composition in lateral as well in depth directions. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is ideally suited to perform this task because it offers elemental as well as molecular information with high sensitivity. A 3-D representation of the sample can be obtained by combining sputter depth profiling and imaging. With modern TOF-SIMS instruments meanwhile a lateral resolution of less than 200 nm and a depth resolution of only a few nm can be obtained. We therefore applied TOF-SIMS to the characterization of commercially available hard disks. We concentrated on the identification of the lubricant present in the uppermost monolayer, screening for corrosion spots and layer structure elucidation. Special emphasis was laid on the automation of measurement and data evaluation routines in order to enhance sample throughput for industrial applications. Examples for spectroscopy, imaging and depth profiling will be presented.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+AS-TuM

Interfaces and Characterization of Organic Thin Films

Moderator: Y. Gao, University of Rochester

8:20am **OE+EM+AS-TuM1 Electronic Properties of Organic Semiconductor Interfaces***,* ***I.G. Hill****,* Princeton University*; C. Shen,* Princeton University, US*; D. Markiewicz, J. Schwartz, A. Kahn,* Princeton University **INVITED**

The alignment of molecular energy levels at the interfaces of organic semiconductor films plays a critical role in determining organic light emitting device (OLED) efficiencies. At a metal/semiconductor interface, the positions of the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO respectively) relative to the metal Fermi level determine the barriers for charge injection into the organic. At organic/organic heterointerfaces, the relative alignment of the HOMO and LUMO levels of the two organics determines whether charges will flow freely across the interface or result in charge accumulation. It is now widely accepted that vacuum levels do not, in general, align at metal/organic interfaces,@footnote 1,2@ implying that techniques such as ultraviolet photoelectron spectroscopy (UPS) and internal photoemission must be used to determine barrier heights. Vacuum levels do align at the majority of organic/organic heterointerfaces, with a few notable exceptions.@footnote 3@ Using UPS, we have studied a variety of both metal/organic and organic/organic interfaces with the goal of understanding the origin of, and therefore ways to control, the interface dipoles which result in vacuum level discontinuities. The results of these studies will be discussed with an emphasis on our attempts to understand the roles of surface modifying procedures, such as oxygen plasma treatment of indium tin oxide (ITO), on improving device performance. @FootnoteText@ @footnote 1@H. Ishii and K. Seki, IEEE Trans. Electr. Devices 44, 1295, (1997) @footnote 2@I.G. Hill, A. Rajagopal and A. Kahn, Appl. Phys. Lett., 73, 662, (1998). @footnote 3@I.G. Hill and A. Kahn, Proceedings of SPIE, Organic Light-Emitting Materials and Devices II, 3476, 168, (1998).

9:00am **OE+EM+AS-TuM3 Photoemission Characterization of Al/Alq@sub 3@ and Al/LiF/Alq@sub 3@ Interfaces***,* ***L. Yan****, Q.T. Le, Y. Gao,* University of Rochester*; M.G. Mason, C.W. Tang,* Eastman Kodak Company

We have investigated the interface formation of Al on tris-(8-hydroxyquinoline) aluminium (Alq@sub 3@) and Al on LiF/Alq@sub 3@ using X-ray and ultraviolet photoemission spectrascopy (XPS and UPS). We observed significant modifications of O1s, N1s and Al2 p core level spectra as Al was directly deposited on the Alq@sub 3@ surface. The Alq@sub 3@ features in the UPS spectra were also quickly destroyed. In contrast, a dramatically different behavior was observed for Al on the LiF/Alq@sub 3@ interface. With o nly 5Å of LiF deposited on the Alq@sub 3@ surface as a buffer layer, the reaction between Al and Alq@sub 3@ is significantly suppressed. A well-defined gap state is formed. The Alq@sub 3@ features in UPS shift to higher binding energies but remain easily recognizable. Both the core level spectra and the gap state suggest that the Alq@sub 3@ anion is formed in the presence of Al and LiF.

9:20am **OE+EM+AS-TuM4 Charge Injection vs. Chemical State of Electrode Surfaces in Metal/Alq@sub 3@/Metal Structures***,* ***C. Shen****,* Princeton University, US*; I.G. Hill, A. Kahn,* Princeton University

The effect of the deposition sequence on the electrical behavior of metal-organic interfaces is an important issue in the context of multiple layer organic light emitting devices (OLED). Metals deposited on organics generally lead to more extensive interface chemistry, and have been reported to produce different electrical behavior, than organics deposited on metals. To address this issue, we investigate the interface chemistry, electronic structure and electrical transport in nominally symmetric Mg:Ag/8-hydroxyquinoline aluminum(Alq@sub 3@)/Mg:Ag structures fabricated and tested in ultra-high vacuum and under controlled atmosphere. We perform detailed X-ray photoemission spectroscopy measurements which confirm that the metal-organic chemical reaction and interdiffusion are different at the Mg-on-Alq@sub 3@ interface than at the of Alq@sub 3@-on-Mg interface. We also show, however, that the chemical state of the bottom electrode surface plays a major role in the device electrical behavior. The Mg:Ag/Alq@sub 3@/Mg:Ag structure built in ultra-high vacuum leads to symmetric top and bottom electron injection, whereas controlled oxidation of the bottom metal surface leads to a two-order-of-magnitude lower bottom contact injection. These results fully explain earlier results obtained for devices made under "standard" conditions, i.e. in moderate 10@super -5@ Torr vacuum. A similar study of the Al/Alq@sub 3@/Al structure is under way and will be reported as well at the conference.

9:40am **OE+EM+AS-TuM5 Investigation of the Electronic Structure of Organic Schottky Contacts with Photoemission Spectroscopy: Discrimination Between Interface Dipole, HOMO Offset, Band Bending and Charging Related Spectral Shifts***,* ***R. Schlaf****, G.P. Kushto, L.A. Crisafully, C.D. Merritt, Z.H. Kafafi,* US Naval Research Laboratory

We have determined the electronic structure of several organic Schottky contacts formed between the organic luminescent semiconductor tris (8-hydroxyquinolinato) gallium (Gaq@sub 3@) and the metals Al, Mg, Ag, Au, and Pt. The investigated interfaces were prepared by vapor deposition of Gaq@sub 3@ on in-situ deposited metal films or thin sputtered high purity metal foils in a multi step growth procedure. Before growth and after each Gaq @sub 3@ deposition step the samples were characterized in situ using a combination of x-ray and ultraviolet photoemission spectroscopies (XPS, UPS). UPS was used to measure the highest occupied molecular orbital (HOMO) positions and interface dipoles, while XPS was used to determine the band bending (bulk charge redistribution) at the interface. In addition, simultaneous measurements of the high binding energy cutoff of the XP- and UP-spectra allowed the determination of the onset of charging phenomena observed at around 100Å Gaq@sub 3@ film thickness. Our results demonstrate that both, charging and band bending effects, may result in strong shifts of the PES spectra which need to be carefully evaluated in order to accurately determine the orbital line-up and the dipole at the interface. Our experiments suggest that the investigated organic Schottky contacts have large interface dipoles due to the chemisorption of the first organic layer in contact with the metal surface. All investigated interfaces also exhibit strong band bending in the organic layer, which strongly depends on the work function difference between Gaq@sub 3@ and the particular metal in contact.

10:00am **OE+EM+AS-TuM6 Examination of Band Bending at Organic Semiconductor / Metal Interfaces Studied by Kelvin Probe Method*, H. Ishii,* *N. Hayashi, E. Ito, K. Seki,* Nagoya University, Japan

How the energy levels of an organic semiconductor and a metal electrode align at the interface between them is a critical and basic issue for understanding organic electronic devices. So far, Mott-Schottky (MS) model has been applied for the estimation of the electronic structure at organic/metal interfaces. In the model, vacuum level alignment is assumed right at the interface, while the Fermi level alignment is achieved through band bending in space charge layer. In order to examine the validity of this model, the film-thickness dependence of the location of the vacuum level of TPD (N,N'-bis(3-methylpheyl)-N,N'-diphenyl-[1,1'-biphenyl]-4,4'-diamine) on various metals(Au, Cu, Ag, Mg and Ca) were measured by Kelvin probe method in ultrahigh vacuum (UHV). At all the interfaces, an abrupt shift of the vacuum level was observed within 1 nm thickness, while further deposition of TPD up to 100 nm led to no change of the location of the vacuum level. These results indicate that the possible space charge layer is much thicker than 100 nm in UHV. The observed relation between the vacuum level shift and the work function of the metals suggests that (1) the Fermi level of TPD is located around the midgap in UHV condition and that (2) the Fermi level alignment is achieved only at TPD/Cu,Ag,Mg interfaces, not by band bending but by dipole layer formation right at the interface. These findings clearly demonstrate the invalidity of MS model for organic / metal interfaces in UHV. The results for the interface between Alq@sub 3@ (tris(8-hydroxyquinolino)aluminum) and metal will be also presented.

10:20am **OE+EM+AS-TuM7 Schottky Energy Barriers and Charge Injection at Metal/Organic Interfaces*, I.H. Campbell,*** Los Alamos National Laboratory*; B.K. Crone,* Lucent Technologies*; R.L. Martin, D.L. Smith,* Los Alamos National Laboratory*; C.J. Neef, J.P. Ferraris,* University of Texas, Dallas **INVITED**

We present independent measurements of metal/organic Schottky energy barriers and their charge injection characteristics in metal/organic/metal structures. The Schottky energy barriers were measured using internal photoemission and built-in potential techniques. The Schottky energy barriers to a poly (p-phenylene vinylene) based polymer (MEH-PPV) and to Alq were measured for a variety of metals with work functions ranging from 2.7 eV (Sm) to 5.6 eV (Pt). For MEH-PPV we find good agreement with the ideal Schottky model. In contrast, for Alq we find that the ideal Schottky picture is not applicable and that electron injecting contacts are pinned about 0.6 eV below the electron conducting states. The charge injection characteristics of these contacts were investigated by measuring the current-voltage characteristics of single carrier structures. The dependence of the current-voltage characteristics on the Schottky energy barrier is quantitatively described by a device model which includes charge injection, transport and space charge effects in the structure. For Schottky barriers less than about 0.3 eV the current in the structure is space charge limited and the contact is ohmic. Finally, we present results using organic self-assembled monolayers to manipulate the metal/organic Schottky energy barrier and to control charge injection into the organic material. The monolayers are used to insert a thin (1 nm) dipole layer between the metal contact and the organic material. Depending upon the orientation of the dipole layer the Schottky energy barrier may be increased or decreased and the corresponding charge injection properties degraded or enhanced.

11:00am **OE+EM+AS-TuM9 Interfacial Electronic Structures between p-Sexiphenyl and Metals Studied by Electron Spectroscopies*, E. Ito,*** *H. Oji, H. Ishii, Y. Ouchi, K. Seki,* Nagoya University, Japan

Recently, organic electroluminecent (EL) devices have attracted much attention in relation to application to flat panel display. In order to understand the charge injection mechanism in such devices, the energy level alignment at the interfaces between organic films and metal electrodes is of crucial importance. In this study, we investigated electronic structures at the interfaces between p-sexiphenyl (6P) and a metal (Au or Mg) by ultraviolet photoelectron spectroscopy (UPS), metastable atom electron spectroscopy (MAES), and X-ray photoelectron spectroscopy (XPS). MAES is an extremely surface sensitive method because the excitation source is metastable atoms which can not penetrate into a sample. The abrupt shift of the vacuum level by 6P deposition on the evaporated metal film (Au or Mg) was observed in the UPS spectra. MAES spectrum of 6P on Au with the thickness of 0.3nm is almost similar with that of 20nm thick 6P film. This suggests that the flat-lying 6P molecules uniformly covered Au substrate. We also measured the spectra of Au on 6P/Au. Even when Au was evaporated with the thickness of 50nm, the spectral feature of 6P dominates in the MAES spectra, suggesting that Au does not cover completely with the 6P film, while the core level peak of Au gradually increased in XPS spectra with deposition of Au. Similar trend was also observed for Mg deposited on 6P/Mg. These results indicate the diffusion of Au into 6P film, leading to formation of the intermixing region. In the system of Au on 6P film, we observed downward shift of the energy levels with irradiation of UV-light (the excitati on source of UPS), probably due to the photovoltaic effect. These results show the the formation of the different interface between the 6P/metal and the metal/6P.

11:20am **OE+EM+AS-TuM10 A Photoemission Investigation of Interfaces of poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) with an oligomer (p-sexiphenyl) and a Metal - Calcium*, A. Rajagopal,*** Univ. Notre-Dame, Belgium*; N Koch,* Tech. Univ. Graz, Austria*; J Ghijsen,* Univ. Notre-Dame, Belgium*; K. Kaeriyama,* Kyoto Inst. of Tech., Japan*; R.L Johnson,* Univ. Hamburg, Germany*; G. Leising,* Tech. Univ. Graz, Austria*; J.J. Pireaux,* Univ. Notre-Dame, Belgium

Poly(2, 5-diheptyl-1,4-phenylene-alt-2,5-thienylene) (PDHPT) is a blue light emitting conjugated polymer with a band gap of ca. 3 eV, and is a promising candidate as an active material in organic light emitting diodes. The interface of this polymer with a) a blue light emitting oligomer (sexiphenyl- 6P), and with b) a low work function cathode material, calcium (Ca) have been investigated using both ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS). Both 6P and PDHPT have a band gap of ca. 3 eV, as well as similar ionization potentials, and this makes the interface an interesting one. A systematic study of the in-situ growth of 6P on PDHPT allows the estimation of the relative positions of the HOMOs and the vacuum levels. We find that the HOMO of PDHPT is below that of 6P, and there is a vacuum level offset of 0.3 eV suggesting charge transfer from 6P to PDHPT. In the case of metal-PDHPT interface, Ca was deposited in extremely small steps in-situ, and both XPS and UPS data were recorded after each subsequent deposition. Contrary to what can be predicted based on calculations and experiments on similar systems, namely phenylenes and thiopehenes, we propose that Ca forms covalent bonds with the polymer. The consequences of these experimental findings will be discussed within the context of LEDs.

11:40am **OE+EM+AS-TuM11 A Photoelectron Study of Chemically Treated Indium Tin Oxide Surface and Its Reactivity with Phenyl-Diamine*, Q.T. Le,*** *F. Nuesch, E.W. Forsythe, L.J. Rothberg, Y. Gao,* University of Rochester

We report on the effect of various treatments by base and acid solutions on the work function of indium tin oxide (ITO). Ultraviolet and x-ray photoelectron spectroscopy (UPS and XPS) were used to measured the work function and chemical composition, respe ctively, of the processed ITO surface. The results indicate that the magnitude of the work function shift is highly dependent on the nature of the solution. In contrast, for the same solution, the concentration of the solution appears to have little effe c t on the work function shift. In addition, the interface formation between processed ITO and N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB) using XPS and UPS is presented. The reactivity of the treated ITO surfaces versus NPB is co mp ared with the case of plasma-treated sample. The low current onset obtained from the single-layer devices based on acid-treated ITO can be attributed to the low energy barrier for hole injection at the ITO/hole-transporting material interface. This work was supported in part by DARPA DAAL 0196K0086, NSF Grant DMR-9612370, and the Swiss National Science Foundation.

Applied Surface Science Division
Room 6A - Session AS-TuA
Modeling in Applied Surface Science

Moderator: C.S. Fadley, Lawrence Berkeley National Laboratory

2:20pm **AS-TuA2 A Microscopic View of Energetic Desorption Events***, **B.J. Garrison**,* Pennsylvania State University **INVITED**

Molecular dynamics computer simulations have been used to model desorption processes of energetic particle bombardment (SIMS, FABMS) as well laser ablation of organic films (MALDI). The results of the simulations are used to compare with experimental data and to provide microscopic insight into the fundamental events. The particle bombardment examples to be discussed include energy and angular distributions of ejected metal atoms and benzene molecules, mechanisms of ejection of organic molecules, and bombardment by cluster projectiles. Topics to be discussed from the laser ablation studies include microscopic mechanisms of ablation, an analytic expression of the velocity distribution of the plume and conditions for desorption of large molecules as in MALDI experiments. Further information can be found at http://galilei.chem.psu.edu/.

3:00pm **AS-TuA4 Theory of Multi-Atom Resonant Photoemission***, **F.J. Garcia de Abajo**, C.S. Fadley, M.A. Van Hove,* Lawrence Berkeley National Laboratory

Multi-atom resonant photoemission (MARPE) takes places when a core electron of a solid can be excited by an incoming photon beam via two different channels: direct photoexcitation and resonant excitation of a nearby atom that decays via inter-atomic interaction giving rise to the emission of the same core electron. This process permits one to detect the presence in the sample of neighboring atoms A and B of different atomic identity by observing the photoemission signal coming from atom A when the photon energy runs across an absorption edge of atom B. MARPE has been recently observed in several materials, including alloys and multilayered surfaces. A theory of this phenomenon is described here showing good agreement with experiment.

3:20pm **AS-TuA5 Oxide-free Phosphate Films on Metals probed by Core and Valence Band X-Ray Photoelectron Spectroscopic Studies in an Anaerobic Cell***, J.A. Rotole, **P.M.A. Sherwood**,* Kansas State University

This paper will show how clean metal surfaces can be reacted via aqueous electrochemical treatment in an anaerobic electrochemical cell to yield a phosphate film that can be directly attached to the metal surface without the presence of any intervening oxide. Such oxide-free films have the potential to serve as a corrosion inhibiting film, and may have other applications such as in the formation of biocompatible surfaces. Previously published work on aluminum and iron will be discussed but the focus of the paper will be new studies on copper. The work illustrates how it is essential to start with an oxide-free metal surface and to perform the treatment in an inert environment in an anaerobic electrochemical cell using aqueous phosphoric acid. It will also be seen that valence band photoemission, interpreted by band structure and other calculations, is a very effective tool for conclusively identifying the surface species present, and in particular distinguishing between oxide and phosphate surface films. This material was based upon work supported by the National Science Foundation under Grant No. CHE-9421068.

3:40pm **AS-TuA6 Spatial Resolution in Scanning Auger Microanalysis of Complex Systems***, **A.L. Linsebigler**,* General Electric Corporate Research and Development Center

Auger electron spectroscopy is one of the primary surface analytical tools in industrial laboratories. The introduction of analytical instrumentation with field emission sources has expanded the capabilities of Auger analysis to include sub-micron phase and particle identification. The spatial resolution of scanning Auger microanalysis is always in question, especially for complex samples such as alloys and multi-component systems. The primary beam size, the primary beam voltage, and the material under investigation are some of the variables which limit the spatial resolution of Auger electron spectroscopy. This study examines the interfacial resolution of metal films with atomic number differences ranging from delta Z = 6 to 65 as a function of primary beam voltage. The interfacial resolution of practical samples such as intermetallic/metal and oxide/metal combinations are also examined. The experimental results will be compared to predictions made by Monte Carlo simulations of electron - solid interactions.

4:00pm **AS-TuA7 Atomic Level Characterization of Metal-Ceramic Interface Energetics and Dynamics via Ab Initio Methods***, **E.A. Carter**, A. Christensen, E. Asche,* University of California, Los Angeles **INVITED**

This talk will be divided into a progress report on ab initio theoretical methods that have been developed to characterize the behavior of interfaces at the atomic level followed by applications of first principles techniques to applied problems. First, w e will discuss a newly developed systematic and accurate theory of adsorption energetics on metals. Second, we will present calculations aimed at understanding the adhesion and ultimate spallation of ceramic coatings on metals. Thermal barrier coatings us ed in high temperature mechanical applications consist of ceramics that are generally spray-coated onto alloy metal surfaces. We will show how one can learn about the interfaces in such materials at the atomic level, via first principles electronic structure techniques. In particular, we will discuss results and insights gleaned from examining surfaces and thin films of ZrO2, Al2O3, their interactions with each other, as well as with Ni surfaces.

4:40pm **AS-TuA9 Surface Science Studies of Model Ziegler-Natta Polymerization Catalysts***, G.A. Somorjai, **S.H. Kim**,* University of California at Berkeley

Model Ziegler-Natta catalysts of titanium chloride, supported on Au and MgCl@sub 2@, have been synthesized using chemical vapor deposition (CVD) methods in a ultra-high vacuum (UHV) chamber and tested for polymerization of ethylene and propylene with triethylaluminum, AlEt@sub 3@, as a co-catalyst in a high-pressure reaction cell. The deposition kinetics, chemical composition, surface sites, and activation of model catalysts are investigated using Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and temperature-programmed desorption (TPD). TiCl@sub 4@ does not chemisorb on either Au or MgCl@sub 2@ to form a film stable at room temperature in UHV. The titanium chloride films supported on Au (TiCl@sub x@/Au) are produced by electron beam irradiation onto the substrate during the TiCl@sub 4@ exposure. Electrons induce the ionization and dissociation of TiCl@sub 4@, producing active species that can be deposited on Au at both 100K and 300K. The deposition temperature alters the stoichiometry and structure of TiCl@sub x@/Au due to difference in deposition kinetics. The titanium chloride films supported on magnesium chloride (TiCl@sub x@/MgCl@sub 2@/Au) are prepared by reaction of TiCl@sub 4@ with Mg on Au. Two deposition sequences, co-deposition of gas-phase Mg and TiCl@sub 4@ and deposition of TiCl@sub 4@ on a Mg film, are used. Regardless of deposition sequence, the uppermost layers of the TiCl@sub x@/MgCl@sub 2@/Au films are mostly composed of titanium chloride, though the distribution of titanium chloride in the film changes with deposition sequence. For these model catalysts before and after the AlEt@sub 3@ treatment, desorption behaviors of organic molecules are studied to differentiate various adsorption sites on the surface. Identification of active sites for polymerization will be attempted from the comparison of the distribution of surface sites with polymerization activity.

5:00pm **AS-TuA10 Dynamic Monte Carlo Simulations of Catalytic Surface Reactions: CO + NO on Rhodium***, **J.W. Niemantsverdriet**, M.J.P. Hopstaken, J.J. Lukkien, A.P.J. Jansen, P.A.J. Hilbers,* Eindhoven University of Technology, The Netherlands

A Dynamic Monte Carlo simulation procedure which succesfully describes diffusion, adsorbate interactions, island formation and reconstructions, has recently been described.@footnote 1@ We have used this approach to describe adsorption, desorption and dissociation of NO, as well as reactions between CO and NO on Rh(111) and Rh(100). When NO is adsorbed on Rh(111), TPD shows that the saturation increases from 0.68 ML at 150 K to a 0.75 ML at 225 K.@footnote 2@ This is accompagnied by ordering of the adsorbate layer, as evidenced by LEED. These phenomena are accounted for by a delicate interplay between mobility of and lateral interactions between NO molecules. We have also used Monte Carlo techniques to simulate recent experimental results on NO adsorption at elevated temperatures, where NO adsorbs both dissociatively and molecularly. Static SIMS shows that dissociation starts at 250 K and continuously increases up to 350 K. These experimental observations are satisfactorily explained in the model by adding pairwise repulsive interactions between neighbouring adsorbed species, which increases the activation barrier for dissociation. Similar effects play a role in the explosive reaction between CO and NO on fully occupied surfaces. In addition to repulsive interactions, fast diffusion of adsorbed molecules appears to be essential to reproduce explosive behavior in the simulations. The key point is that for a realistic description of repulsion between adsorbates, one has to consider the local environment of an adsorbed atom or molecule. @FootnoteText@ @footnote 1@ R.J. Gelten, A.P.J. Jansen, R.A. van Santen, J.J. Lukkien, J.P.L. Segers, P.A.J. Hilbers, J. Chem. Phys. 108 (1998) 5921. @footnote 2@ R.M. van Hardeveld, M.J.P. Hopstaken, J.J. Lukkien, P.A.J. Hilbers, A.P.J. Jansen, R.A. van Santen, J.W. Niemantsverdriet, Chem. Phys. Lett. 302 (1999) 98.

Organic Electronic Materials Topical Conference
Room 616/617 - Session OE+EM+AS-TuA

Organic Thin Film Growth

Moderator: H. Baessler, Philipps Universität, Germany

2:00pm **OE+EM+AS-TuA1 Tailoring of Properties of Organic Thin Films by Interface Control**, ***E. Umbach****, M. Sokolowski, R. Fink,* Universität Würzburg, Germany **INVITED**

The properties of ultrathin organic films in organic/inorganic hybrid systems are largely determined by their interfaces. This is particularly true for the electronic and structural properties which depend on chemical bonding and ordering processes. In favourable cases weak chemisorption on smooth single-crystal surfaces leads to long-range lateral order, and even true epitaxial growth of organic overlayers can be achieved. For such structurally well-defined films significantly improved transport and optical properties can be expected. It will be shown how high-quality organic thin films can be prepared by vapour-deposition on suited substrates and how the observed superstructures depend on the molecular shape and the functional groups, on the substrate material and orientation, and on the preparation parameters. Moreover, based on a few examples it is demonstrated that epitaxial growth with huge domains and even with new, substrate-induced structural parameters can be achieved. In view of their optical properties, for instance, such films show very few defects, considerably improved quantum efficiency, and reduced substrate-induced quenching. The knowledge about the various properties and their interdependences has been achieved by combining a number of surface-sensitive methods for studying the geometric (STM, (SPA)LEED), chemical (XPS, TDS, HREELS), orientational (NEXAFS), and electronic (UPS, NEXAFS) properties with in-situ measurements of the optical and electric properties. As substrates different metal (e.g., Ag, Ni, Cu) and semiconductor surfaces (Si, Ge, ZnSe, HOPG) have been investigated, and the properties of more than 20 different large organic molecules have been compared. On the basis of the present results one can now start to tailor the properties of ultrathin organic films by selecting a proper combination of molecules, substrates and preparation conditions.

2:40pm **OE+EM+AS-TuA3 Ordering in Two Dimensions - Phthalocyanines, Perylenes, and Related Molecular Thin Films**, ***N.R. Armstrong,*** University of Arizona **INVITED**

Well-ordered two-dimensional thin films can now be routinely produced by either vacuum deposition and/or self-assembly deposition technologies, and rules for epitaxial growth of such materials on a variety of single crystal substrates are becoming well understood. This talk will review recent work on the growth of both phthalocyanine and perylene dye thin films, on both single crystal metal and nonmetal surfaces. Many of the crystalline organic dyes tend to form flat-lying ordered monolayers, with coincident epitaxial relationships with the substrate. Several interesting cases have recently emerged, however, where such flat-lying monolayers are not formed, and/or where neither coincident nor commensurate epitaxial structures are formed, but ordered films result nevertheless. In all events organic heterojunction formation is of interest for these materials, and characterization of such heterojunctions by combinations of XPS/UPS will be discussed. In addtion, we will discuss recent self-assembly approaches to ordered phthalocyanine thin films, by non-vacuum deposition approaches, which produce coherence in thin film structures rivaling the best vacuum deposited materials.

3:20pm **OE+EM+AS-TuA5 Influence of Steps on the Orientation of Monolayer Films of Copper Phthalocyanine (CuPc) on Au(111)**, ***I. Chizhov****, A. Kahn, G. Scoles,* Princeton University

The structure of monolayer films of copper phthalocyanine (CuPc) deposited on Au(111) surface in ultrahigh vacuum is studied via scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). CuPc molecules adsorb with the molecular planes parallel to the surface and form a highly ordered overlayer with a square unit cell. The structure of the CuPc molecular layer is analyzed via correlation of STM and LEED data. The azimuthal orientation of the monolayer is found to be distinctly different on wide and narrow terraces of the Au(111) substrate. On wide terraces the azimuthal orientation of the monolayer is determined by the underlying substrate with the sides of CuPc square unit cells aligned within a few degrees off the [11(bar)0] and [112(bar)] directions of the Au(111) surface. On the other hand, on narrow terraces and in the vicinity of the Au substrate steps the sides of CuPc unit cells are aligned along the step edges. Thus, CuPc/Au(111) represents a good model system for which a balance between the energy of interaction of a molecule with the metal surface and that of interaction with the step edges can be studied in detail. For CuPc films with coverages below and above 1 monolayer no molecular structure can be reproducibly resolved by the STM.

3:40pm **OE+EM+AS-TuA6 Growth Modes of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-Diamine on Standard and Ultra-flat Indium Tin Oxide**, ***E.W. Forsythe****, Q.T. Le, Y. Gao, L.J. Rothberg, M. Abkowitz,* University of Rochester

The ITO substrate morphology influences the growth conditions of N,N'-bis-(1-naphthyl)-N,N'-diphenyl1-1,1-biphenyl1-4,4'-diamine (NPB) for organic light emitting diodes. We have studied the growth modes of NPB on as-received indium tin oxide (ITO) and ultra-flat ITO using atomic force microscopy (AFM). The ITO surface morphology has been reduced from an average area roughness of 1.8nm to less than 0.2nm with clearly distinguishable atomic terraces corresponding to the ITO lattice spacing. The room temperature NPB growth mode is initially islands with complete ITO coverage at 15nm for both ITO surfaces. With a substrate temperature less than 15C above room temperature, the growth modes are laminar with full ITO coverage at 7.5nm. The final NPB film on the ultra-flat ITO has an average roughness equivalent to the size of the NPB molecule, more than an order of magnitude less than NPB on standard ITO. Because NPB is trap free, a direct and self-consistent measure of the injection efficiency as a function ITO surface morphology and growth temperature can be determined at a given applied field from the ratio of the measured dark current to the calculated trap free space charge limited current. The trap free space charge limited current is calculated from the time of flight drift mobility measured in the same specimen at the same applied field.@footnote 1@ The OLED device performance shows an approximately 15% increase in the cd/A efficiency on the ultra-flat ITO as compared to standard ITO. Understanding the role of the ITO surface morphology on OLED device characteristics may contribute to improved large area device performance. This work was supported by DARPA DAAL01-96-K-0086, NSF DMR-9612370, AFOSR 96NL245, and the NSF Center for Photoinduced Charge Transfer. 0. @FootnoteText@ @footnote 1@ M.Abkowitz,J.S.Facci and J.Rehm. J. Appl. Phys. 83, 2670 (1998).

4:00pm **OE+EM+AS-TuA7 Self-Assembled Monolayers on Indium Tin Oxide***, C. Yan, M. Zharnikov,* ***A. Gölzhäuser****, M. Grunze,* Universität Heidelberg, Germany

Self-Assembled Monolayers (SAMs) of functionalized alkanethiols X(CH@sub 2@)@sub n@SH (X=CH@sub 3@, COOH) and carboxylic acid CH@sub 3@(CH@sub 2@)@sub n@COOH were prepared on indium tin oxide (ITO) surfaces and have been characterized by X-ray photoelectron (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopies as well as by Atomic Force Microscopy (AFM). Thiols as well as carboxylic acids form homogeneous, ordered films on ITO. NEXAFS data suggest that the films are molecularly oriented with average alkyl chain tilt angles between ~34° for thiolate and ~31° for bifunctional SH(CH@sub 2@)@sub 15@COOH. From coadsorption experiments we find that on ITO the COOH group adsorbs preferentially over the SH group. AFM and LFM images indicate a smoothing of the relatively rough ITO surface by the adsorbed films. These results suggest that ITO surfaces can be passivated with Self-assembled monolayers and that SAMs can be utilized to covalently attach specific chemical functionalities to ITO electrodes.

4:20pm **OE+EM+AS-TuA8 Mechanism of Formation of Self-Assembled n-Octadecylsilane Monolayers on Indium-Tin-Oxide**, ***K.-W. Lee****, A.M. Raphel, S.L. Buchwalter,* IBM T.J. Watson Research Center*; M.M. Poliks,* IBM Microelectronics

Mechanism of formation of self-assembled n-octadecylsilane monolayers on indium-tin-oxide (ITO) has been studied. n-Octadecyltrimethoxysilane (OTMS) was hydrolyzed to n-octadecylmethoxysilanediol or n-octadecylsilanetriol in isopropanol/water (95/5). The 0.5 % hydrolyzed solution was spin-coated onto ITO substrate and then baked at 85 deg.C for 30 min. The subsequently formed organic layers were analyzed with dynamic contact angles, X-ray photoelectron spectroscopy (XPS) and reflection-absorption infrared spectroscopy (RAIR) and determined to have densely packed SAMs. Its RAIR and XPS spectra indicate that lots of silanol groups are left unreacted at the foot of SAMs and a small amount of unhydrolyzed Si-OCH3 groups may also be present. Silanol groups are expected to interact with each other and ITO surface through hydrogen bonding. The distance between Si atoms can be long enough to have a normal tilt angle (app. 30 deg.) of typical SAMs. Si-OH and Si-OCH3 groups were fully condensed to polysiloxane by further thermal treatment at 230 deg.C for 30 min, as evidenced by the disappearance of the O-H band in RAIR as well as by the decrease of the O1s band corresponding to silanol. The possible structural changes in the SAM driven by this condensation are discussed. In contrast to the fully hydrolyzed OTMS solution, a partially hydrolyzed OTMS solution provided loosely packed monolayers, apparently in islands of densely packed alkyl chains rather than as monotonically diminishing coverage.

4:40pm **OE+EM+AS-TuA9 Growth and Characterization of Poly(arylamine) Thin Films Prepared by Vapor Deposition***, **G.J. Szulczewski**, T. Selby, S. Blackstock,* The University of Alabama

We have synthesized a novel series of redox-gradient poly(arylamines) dendrimers for potential applications in organic-based electronic devices. The thermal properties of these materials have been measured by gravimetric analysis and differential scanning calorimetry. In general, these materials exhibit a glass transition temperature near 100 C and show negligible weight loss below 400 C. Thin films (1-100 nm) of these materials were grown under high vacuum conditions by vapor deposition onto a variety of substrates, including: gold, Si(100), and indium-tin oxide coated glass. Ex situ surface characterization was performed with reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, spectroscopic ellipsometry, and atomic force microscopy. These analyses show the formation of high quality films from the organic precursors with molecular weights exceeding 1300 amu without molecular decomposition. Thus, a new class of functional organic films for potential use in charge storage and transport have been prepared. The efficacy of these films as hole transport materials in electroluminescent devices and charge storage media is under current investigation.

5:00pm **OE+EM+AS-TuA10 HREELS Study of Ultra-thin Polyaniline Films Grown on Cu(110) by Vapor Deposition of Aniline Tetramers***, **K.K. Lee**, J.M. Vohs,* University of Pennsylvania*; N.J. DiNardo,* Drexel University

Substrate-dependent reactivity, thin film polymerization, and metallic conductivity upon doping have been demonstrated in previous HREELS studies of vapor-deposited emeraldine thin films on metal surfaces.@footnote 1@ In those studies, the chemical vapor was composed of a distribution of oligomeric sizes. In this HREELS study, the effect of the size of vapor-deposited oligomers on the growth of polyaniline at a metal surface is addressed through deposition of aniline tetramers on Cu(110). Analysis of vibrational and electronic spectra for growth up to ~70 Angstroms shows polymerization reactions with shorter chain lengths of the resulting polyaniline ultra-thin films than for deposition from emeraldine vapor. Upon doping, the far-infrared region exhibits intense tailing and a plasmon loss indicating that local conductivity is similar to ultra-thin films composed of longer chains. @FootnoteText@ @footnote 1@K. K. Lee - Surf Sci. 420 (1999) L115 and references therein.

Vacuum Metallurgy Division
Room 620 - Session VM+MI+AS-TuA

Magnetic Recording: Head/Disk Interface and Overcoats

Moderator: Y.W. Chung, Northwestern University

2:00pm **VM+MI+AS-TuA1 Ultra Thin DLC Film as Magnetic Disks Overcoat***, **X. Chu**, B. Zhang, K.. Johnson,* MMC Tech.

Sputtered DLC film of 100 to 200 A has been used for protective coating on thin film magnetic recording disk for years. DLC overcoat material of choice is hydrogen and/or nitrogen doped amorphous carbon deposited by magnetron sputtering. Increasing areal density in magnetic hard drives requires thinner overcoat to reduce signal loss between magnetic film and read head. Functional overcoat with thickness of 50A will be needed for next generation recording medium. Tribological performance of sputtered carbon films suffers at values below 100 A because of a degradation in physical properties. Alternative deposition techniques, such as ion-beam deposition process, create denser and harder films with the improved physical and tribological properties. In this paper we will present data on the deposition and characterization of 50 A to 30 A DLC films deposited both by sputter and IBD process. Process parameter effect on structure and mechanical properties of sputtered CNx, CHx film, and ion beam deposited CHx was studied. XPS and Raman were used to characterize film microstructure and showed the sputtered CNx film was mostly sp2 bonded. Tribology of the films were tested by Contact Start Stop (CSS) testers and the result of carbon wear can be correlated to AFM nano-wear test. 30A ion-beam deposited CHx film showed good CSS tribological performance comparable to 100 A sputtered films.

2:20pm **VM+MI+AS-TuA2 Tribological Properties of Protective Carbon Coatings Used in Magnetic Storage Devices Investigated on a Sub-Nanometer Scale***, **A. Wienss**,* University of Saarbrücken, Germany*; G. Persch-Schuy,* IBM Germany Storage Systems Division, Germany*; U. Hartmann,* University of Saarbrücken, Germany

Ultrathin carbon coatings are used in the magnetic storage industry to protect sensitive sensor heads and magnetic media against mechanical damage. Such a damage can be modelled by artificially generated scratches using Scanning Force Microscope (SFM) techniques. Loading forces in the µN range are applied, resulting in scratches with residual depths of only a few Å. A special image subtraction technique is presented which allows careful analysis of tiny grooves even on rough surfaces. This technique compensates for drift effects during scanning. The scratching resistance of various a-C:H and CN@sub x@ films is determined. For a-C:H, an increasing amount of hydrogen results in a decreasing scratching resistance, which is a well-known behavior. Beyond a certain hydrogen content, a further increased hydrogenation causes a reproducible, slight increase of the scratching resistance. In order to explain this, the role of the friction coefficient will be discussed.

2:40pm **VM+MI+AS-TuA3 Ultrathin Overcoats For Magnetic Media: Is Hardness What We Are Looking For ?***, **B. Marchon**,* IBM Almaden Research Center **INVITED**

As areal recording densities approach 20 Gigabit per square inch, the demand for ultrathin media overcoat (<5 nm) becomes more pressing. This talk will attempt to identify the various properties that are required to achieve good performance under increasingly severe mechanical and environmental conditions. In an attempt to bridge the process-performance gap, we will review the details of the head/disk interface system, and how the mechanical and chemical structure/properties can be optimized to achieve the required reliability. In particular, issues related to tribochemistry and interactions with the lubricant will be addressed, as well as a general discussion on what specific mechanical properties are important.

3:20pm **VM+MI+AS-TuA5 Air Bearing Collision Dynamics***, **S.E. Stupp**, R.J. Blanco, T. Riener, B.D. Strom,* Quantum Corporation **INVITED**

A few years ago, a disk drive program encountered an unusual problem: drives built with one vendor's heads (vendor A) suffered from an excessive number of thermal asperity events (TAs); drives built with head's from another vendor (vendor B) did not have as many TAs, but they did have a number of crashes. Spinstand experiments confirmed that there was a significant difference in the response of the two vendor's air bearings to collision with the 100 nm high asperities found in these drives. For example, the fly height of vendor A's heads was essentially unchanged on contact with an asperity, while vendor B's heads exhibited a fly height change (these differences may explain the drive results). The underlying problem in the drive program was ultimately traced to particulate contamination and was corrected. However, the experiments raise an interesting question: Why is there a difference in the dynamic response of the two vendor's heads? In this work we present a systematic study of this problem, which we christen Air Bearing Collision Dynamics (ABCD). The asperity collision responses of several different air bearing designs (including full rail and island type) were studied by measuring the TA signal, the change in flying height, acoustic emission (AE), and laser Doppler vibrometry, in controlled experiments on a spinstand. Since a large enough asperity can cause any head to crash, the asperity size was modest (approximately equal to the fly height). In agreement with our earlier experiments, differences in the response of the different air bearings were found. In addition, the AE signals indicate that certain island type air bearing designs can undergo multiple head-disk contacts after the asperity has passed. These results are potentially concerning, because many head vendors are moving towards this type of air bearing design. Finally, in an attempt to understand the origin of the differences in the dynamic response of different air bearing designs, we report the results of numerical modeling of the asperity and air bearing designs.

4:00pm **VM+MI+AS-TuA7 Interaction of Fluoroalcohols and Fluoroethers with Various Types of Carbon Overcoats***, **N. Shukla**, A.J. Gellman,* Carnegie Mellon University

This work is focussed on understanding the fundamentals of head-disk interface tribology at very low flying heights and higher spin rates. Since there will be room for only a single molecular monolayer of the lubricant on the disk surface at low flying heights we have studied the molecular level interaction of lubricants with carbon overcoats that protect the disk surface. We have modeled a most commonly used PFPE lubricant (Fomblin Zdol) using short chain model compounds and measured the desorption energy of these compounds on carbon films. The short chain model compounds used are 2,2,2 trifluoroethanol (CF@sub3@CH@sub2@OH) and perfluorodiethyl ether (CF@sub3@CF@sub2@OCF@sub2@CF@sub3@) which are representative of both the end group and the main chain of Fomblin Zdol. Temperature programmed desorption spectroscopy is used to measure the desorption energy of model compounds and also to understand the nature of the interaction of these short chain compounds with carbon overcoats. Initial results show that ethers interact with carbon overcoats through electron donation from the oxygen lone pair electron and the alcohols interact with carbon overcoats through hydrogen bonding. In addition we have studied the effect of various film compositions on the interaction of the lubricants in order to understand if the film composition has any effect on the nature of the bonding of the lubricant. The different types of overcoats used are hydrogenated, nitrogenated, diamond-like carbon and Ion beam sputtered overcoats. We have observed that by varying the percentage of hydrogen or nitrogen content in the film composition or by changing the carbon overcoat deposition conditions as in diamond like carbon overcoats or in an ion beam sputtered overcoat there is no significant change in the interaction of the lubricant with carbon overcoat. The alcohols however bond stronger than ethers on all overcoats, which is consistent with the structures, proposed by diffusion measurements.

4:20pm **VM+MI+AS-TuA8 Angle Resolved ESCA Methods: Molecular Conformation of Fluorocarbon Lubricant***, **M.A. Karplus**, D.J. Pocker,* IBM-SSD

Simple but useful methods for interpreting angle-resolved ESCA data from real-world samples are presented. First is a model allowing thinly-covered and thickly-covered substrate. It can be usefully applied, even in a manual fashion, with common office spreadsheets. Next, a simple slab model, with the help of canned minimization routines, can bring out subtleties in overlayer structures. Even a deeply buried monatomic layer can be isolated. The following are presented as examples. Perfluoropolyether (Zdol) lubricant on hard disk carbon overcoat shows coexisting monolayer and multilayer regions, consistent with structures identified by surface energy@footnote 1@ and ellipsometric surface diffusion@footnote 2@ measurements. Next, layering within the lubricant shows significant perfluoropolyether backbone adjacent to the overcoat surface accompanied by a discernible excess of ether oxygen. The latter facts indicate that the inverted-U conformation sometimes sketched for bonded lubricants is an exaggeration, certainly for the system studied. @FootnoteText@ @footnote 1@ G. W. Tyndall, R. J. Waltman, and D. J. Pocker, Langmuir 14, 7527 (1998). @footnote 2@ X. Ma, J. Gui, L. Smoliar, K. Grannen, B. Marchon, M. S. Jhon, C. L. Bauer, J. Chem. Phys. 110, 3129 (1999).

4:40pm **VM+MI+AS-TuA9 Airbearing Designs for High Density Recording***,* **INVITED**

Applied Surface Science Division
Room 4C - Session AS-TuP
Poster Session

AS-TuP1 Pattern Measurements of Reticles with Optical Proximity Correction Assist Features Using the Atomic Force Microscope*, K.-J. Chao,* ***R.J. Plano****, J.R. Kingsley,* Charles Evans & Associates*; F. Chen, R. Caldwell,* MicroUnity Systems Engineering, Inc.

A 4X, 6-inch reticle with optical proximity correction (OPC) assist features intended for deep ultraviolet (DUV) exposure was investigated. A set of chrome lines with designed CD (linewidths in this case) from 0.24 to 2.00 microns was profiled by AFM. The goal of this work is to present a method to ensure consistent measurement of chrome lines widths on the reticle. This is done by consistently measuring the line width at the half-height position on the line cross-section, i.e., full width at half maximum (FWHM). defining the boundaries of the line width at the half height locations of the edge steps. Using this method, the CD linearity is found to be within ±20nm over a range of line widths from 2.00 um to 0.4 um. Additionally, the CD uniformity is found to be worse when the widths of the lines are nominally less than 0.4 um.

AS-TuP2 Changes in the Performance of a Cylindrical Mirror Analyzer Induced by Sputter Depth Profiling*,* ***M. Kottke****,* Motorola, Inc

Optimum performance of a cylindrical mirror analyzer (CMA) is dependent upon proper fringe field correction at both ends of the concentric cylinders. In many CMAs this fringe field correction is accomplished with concentric metal rings deposited on the surfaces of solid ceramics which completely seal off the ends of the analyzer. This paper describes the degradation in performance of the analyzer caused by the redeposition of sputtered secondary ions onto the surface of the conical ceramic at the input of the CMA. It will be shown that the time frame of this degradation varies widely from days to months (or even years) depending on the materials being analyzed and the mode of operation of the CMA. It will also be shown that the loss in integrity of the fringe field correction causes large changes in the energy transmission function of the analyzer. Errors in quantitative calculations based on the use of elemental sensitivity factors determined from standards run on a specific instrument at a fixed point in time can therefore be proportionately large. Alternate modes of operation which minimize degradation are presented along with a discussion of alternate fringe field correction schemes.

AS-TuP3 Formation of Dioptase-like Structures in Silica Xerogeles Doped with Copper*,* ***F. Ruiz****, J.R. Martinez-Mendoza,* Universidad Autonoma de San Luis Potosi, Mexico*; J. Gonzalez-Hernandez,* CINVESTAV-IPN, Mexico

Using IR absorption and Raman spectroscopy we have analyzed the incorporation of Cu in SiO@sub 2@ matrix in samples prepared by the sol-gel method. Samples contain Cu at 30 %wt and were studied as a function of annealing temperature. It is found that the heat treatments have a remarkable influence on the structure. With this analysis we inferred that the final structure of the sample contain dioptase-like structures (Cu@sub 6@[Si@sub 6@O@sub 18@]*6H@sub 2@O).

AS-TuP4 Reaction of Fluorocarbon Contaminants with Aluminum Oxides: Inadvertant Fluoride Formation during Low Temperature Plasma Cleaning of Aluminum Alloy Surfaces*,* ***C.E. Moffitt***[1]*, D.M. Wieliczka,* University of Missouri, Kansas City*; C.M. Reddy, Q. Yu, H.K. Yasuda,* University of Missouri, Columbia

Plasma deposited films have shown promise as intermediate adhesion and barrier layers for use in the interface engineering of corrosion protection systems on various materials. The surface treatment of plasma deposited trimethylsilane (TMS) films with fluorocarbon plasmas has been seen to significantly improve the adhesion of certain paints to these films, which are strongly adhered to underlying aluminum alloy substrates. Oxygen plasma cleaning of the alloy surfaces, prior to deposition of the TMS film, is normally employed to remove organic contaminants. During testing, one batch of aluminum panels was processed without the oxygen plasma treatment and exhibited extensive adhesion failures. An investigation of these results shows that low levels of fluorocarbon contaminants readily react with the alloy surface and deposit a carbonaceous layer, which dramatically interferes with the adhesion of the plasma polymer to the alloys. XPS studies show that the presence of even low levels of these contaminants in the chamber, during the oxygen cleaning process, is sufficient to induce the conversion of the surface from oxide to a mixture of oxide and fluoride. When present, this fluoride layer is found to reduce the corrosion resistance of test panels. Support for this work was provided by DARPA under U.S. Air Force contract F33615-96-C-5055.

AS-TuP5 Photodegradation and Direct Patterning of PVDF and P(VDF-TrFE) using Sychrotron-based X-rays*,* ***P.T. Sprunger****, J. Choi, E. Morikawa, H. Manohara,* Louisiana State University

Upon hard and soft X-ray exposure from a synchrotron storage ring, the photodegradation and direct patterning of PVDF and copolymer P(VDF-TrFE) thick and thin films have been studied with ultraviolet photoemission and mass spectroscopy. After exposure of soft white light X-rays (<1 keV) on crystalline, 5 ML P(VDF-TrFE) films, ultraviolet photoelectron spectroscopy reveals that the photodegradation mechanism involves both an increase in the carbon conjugation (single to double bond formation). With increasing illumination amount of white light, new valence band features emerge near and cross the Fermi level. Furthermore, there is an attenuation of the fluorine 2s core-level intensity due to photodetachment. The photodetached components of the copolymer, as detected with mass spectroscopy, are hydrogen, fluorine, and HF. This photodegradation mechanism affords the ability to direct patterning of PVDF and P(VDF-TrFE) using X-rays. Without the use of any reactive chemical gas, a maximum etched depth in excess of 9 mm is achieved using hard X-rays (2 keV to 16 keV) in thick, amorphous films of PVDF. The ability to pattern PVDF, a piezoelectric, pyroelectric and ferroelectric polymer, has potential applications in the areas of micro-sensors, actuators and non-volatile ferroelectric random access memory (NVFRAMS) technology.

AS-TuP6 An Ellipsometric Study of Plasma Deposited Thin Films*,* ***T. El-Agez****, C.E. Moffitt,* University of Missouri, Kansas City*; H.K. Yasuda,* University of Missouri, Columbia*; D.M. Wieliczka,* University of Missouri, Kansas City

Spectroscopic ellipsometry was used to study films produced from a plasma of trimethyl silane gas deposited on silicon substrates. In addition to the as formed plasma film, the film surfaces were treated with either an oxygen or nitrogen plasma. Ellipsometric measurements were made on the films within 1 day after deposition and as a function of time, to determine the influence of atmospheric conditions. Additionally, the films were exposed to ultra-violet light and the changes were again tracked as a function of time. Several models were used to analyze the ellipsometry results with all of them taking into account the silicon substrate and oxide layer. One kept the overall film thickness constant, i.e. the oxide grew into the deposited film. Another assumed the plasma deposited film was stable but with additional film growth due to the oxidation. And the last allowing for both film growth and modification of the plasma film. The results obtained from these models were correlated to x-ray photoelectron spectroscopy results.

AS-TuP7 Surface-attached Polymer Brushes via Physisorbed Monolayers of Macroinitiators*,* ***T. Stöhr***[2]*, J. Rühe,* Max-Planck-Institute for Polymer Research, Germany

Block copolymer adsorption is a frequently used procedure to modify the surface of solid substrates.@footnote 1@ Such systems, usually A-B block copolymers, consist of an anchor block which allows attachment to the substrate surface and a buoy block which carries the desired surface properties. Since one part of the molecule has to have only a weak interaction with the surface and the other a strong one, the two blocks should be rather different from a chemical point of view. This renders the task of finding a suitable solvent process non-trivial. Monolayers prepared by this technique are inherently very thin with thicknesses typically between 3 and 5 nm. The reason for this is a kinetic hindrance for the attachment of polymer chains due to a diffusion barrier created by the already attached molecules. Recently radical polymerization using chemisorbed azo-type initiators has been established.@footnote 2@ In this case the polymer is grown directly at the surface of the substrate. We present a macroinitiator system that allows to create hydrophobic layers on hydrophilic substrate surfaces. Here a hydrophilic anchor block bearing initiator groups is physisorbed to a hydrophilic surface. The hydrophobic buoy block is polymerized in situ resulting in a block copolymer monolayer. A poly(epsilon-caprolactone) macroinitiator containing azo moieties was synthesized and adsorbed to silicon oxide surfaces. The surface-attached monolayer was subsequently used for the polymerization of n-alkyl methacrylates resulting in thicknesses up to 100 nm. By this route the limitations of the block copolymer physisorption process, such as solubility problems of the block copolymer and intrinsic limitations of the layer

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[1] **ASSD Student Poster Competition Participant**

[2] **ASSD Student Poster Competition Participant**

thickness, can be overcome. @FootnoteText@ @footnote 1@ Fleer, G. J.; Cohen Stuart, M. A.; Scheutjens, J. M. H. M.; Cosgrove, T.; Vincent, B. Polymers at Interfaces; Chapman & Hall: London, 1993; Chapter 6. @footnote 2@ Prucker, O.; Rühe, J. Macromolecules 1998, 31, 592.

AS-TuP8 Observing Damage Produced during XPS Measurements*, **M.H. Engelhard**, D.R. Baer, G.C. Dunham,* Pacific Northwest National Laboratory

An increasing amount of studies in our laboratory involve analysis of polymers, self assembled monolayers (SAMS) with different terminations, insulators and other materials for which some properties of the specimens degrade with time during x-ray exposure. When damage is observed, a series of parameter tests are conducted to determine the conditions and time for which reliable data can be collected. In this paper we will report measurements made on SAMS with CH@sub 3@, OH and COOH, as well as some test coupons of PCEMA, PTFE and PVC. Most of these measurements were made on a Physical Electronics Quantum 2000 for which a variety of different x-ray flux densities can be arranged. In addition, the beam can be moved around to examine the regions over which damage occurs. Measurements for COOH terminated SAM show a damage production directly related to the flux per unit area. These, and other results, suggest that damage on many materials is not simply due to specimen heating. However, tests on PCEMA show damage to occur outside the region that was exposed to the x-ray beam. These tests will be described along with a new series of experiments being undertaken to determine if specimen cooling provides a way to decrease specimen damage. This work was conducted in the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facilty sponsored by the U. S. Department of Energy's Office of Biological and Environmental Research.

AS-TuP9 Role of Temperature in the Surface Oxidation Chemistry of IN-738 Superalloy*, **L. Bracho**[1], S. Seal, V. Desai,* University of Central Florida

Super-alloys are used in high temperature industrial applications because of their strength, high resistance to high-temperature oxidation and hot corrosion, and longer durability than other conventional alloys. Although super-alloys possess these characteristics, they are still subjected to high temperature degradation when exposed to aggressive environments. The current research includes the high temperature oxidation behavior of IN-738 at 850, 900, and 950°C in air for a period of 300 consecutive hours. The oxidation kinetics is parabolic in nature. Due to its parabolic nature, the lattice diffusion is prominent in the various oxide formations. This leads to selective oxidation of various elements present in the alloy. The decrease in oxidation rate observed at higher temperatures is due to more alumina formation. The surface oxide formation is investigated using using XPS, AES, XRD, SEM, and EDS. It is expected to find external oxides rich in chromium, aluminum, nickel, and titanium. The thickness of the oxide and the gamma' depleted layers are expected to increase with temperature.

AS-TuP10 Noncontact AFM Imaging of Al-Adsorbed Si(111) Surface*, **S. Orisaka**, T. Minobe, K. Makimoto, Y. Sugawara, S. Morita,* Osaka University, Japan

Recently, several groups including ourselves have reported true atomic resolution imaging using noncontact atomic force microscope (NC-AFM) operating in ultrahigh vacuum. In order to apply the NC-AFM as a scientific tool in variety of fields such as surface science, it is very important to understand the imaging mechanism of the NC-AFM on various sample surfaces. On the Si(111)7x7 reconstructed surface, we clarified that the tip-sample interaction force is dominated by the chemical bonding interaction between the dangling bond out of the Si tip apex and the dangling bond on Si adatom on the surface. In the present experiments, we investigated force interaction between an orbital of a dangling bond out of a Si tip apex and an empty orbital on a sample surface. As a sample surface with empty orbitals, Al-adsorbed Si(111) surface was used. We obtained strong contrast of NC-AFM images on Al-adsorbed Si(111) surface. Furthermore, we observed the characteristic discontinuity in the distance dependence of the frequency shift. So far, similar discontinuity has been observed on Si(111)7x7 surface, and it can be explained by the chemical bonding interaction between the dangling bond out of the Si tip apex and the dangling bond on Si adatom. So, the discontinuity in the distance dependence of the frequency shift on Al-adsorbed Si(111) surface seems to be originated from the chemical bonding interaction between an orbital of a dangling bond out of a Si tip apex and an empty orbital on a sample surface.

AS-TuP11 Characterization of Chemically Heterogeneous Samples Using XPS Imaging and Small Area Analysis*, **A.C. Ferryman**[2], J.E. Fulghum,* Kent State University

Recent advances in XPS instrumentation allow for the rapid acquisition of photoelectron images with a spatial resolution of a few microns. This capability both expands the range of samples which can be characterized using XPS, and provides additional complications in data interpretation and analysis. For samples which have a surface roughness comparable to the depth- of-focus within the image, care must be taken to distinguish between surface roughness effects and changes in chemical state or elemental distribution. Sandstones coated with a commercial perfluoropolyether for protection from weathering were characterized using imaging and small area XPS. Polymer impregnation into the stone, and uniformity of the polymer coating were characterized through analysis of both cross-sections and the surface of the sandstone. Variations in polymer distribution on both macro- and micro-scales will be discussed and evidence for polymer segregation between components of the sandstone evaluated. This system provides an example of the information which can be obtained, and artifacts which must be considered, in the analysis of a chemically heterogeneous sample which also contains significant surface roughness.

AS-TuP12 Characterisation of Oxide on GaAs Wafer Surfaces with TOF-SIMS and ARXPS*, **B. Burkhardt**, O. Brox,* Universität Münster, Germany*; W. Fliegel,* Freiberger Compound Materials GmbH, Germany*; L. Wiedmann,* Universität Münster, Germany*; A. Kleinwechter,* Freiberger Compound Materials GmbH, Germany*; A. Benninghoven,* Universität Münster, Germany

Molecular-beam epitaxy (MBE) on GaAs requires a thermally removable oxide. Therefore reliable techniques are needed to control oxides on the GaAs wafer surface in the production process. The quantitative oxide characterization (thickness and stoichiometry) can presently only be achieved by ARXPS. In this paper we compare results achieved with TOF-SIMS and ARXPS. The experiments were performed in a reflectron based TOF instrument equipped with an 8'' manipulator for macroscanning and a dual beam source for depth profiling (sputter beam: 500eV Cs@super +@, analysis beam: 10kV Ar@super +@). For ARXPS we used a spherical electron analyzer with multichannel detector and monochromator X-ray source (Al K@alpha@: 1486,6 eV). For ARXPS data interpretation we assumed a 4-layer-system for the GaAs oxide. Separating the XPS signal into different oxide states we determined thickness and stoichiometry of each layer. Dual beam depth profiling was used to characterize the oxide layer by means of SIMS. The integrals of the secondary ions AsO@sub n@@super -@ and GaO@sub n@@super -@ over the sputter depth can be correlated to the oxide thickness and the various oxide phases as identified by ARXPS. The use of SF@sub 5@@super +@ primary ions allowed the detection of Ga@sub m@As@sub n@@super ±@ cluster ions with more than 40 atoms. The Ga/As ratio of these clusters changes with storage time and can be taken as a measure of stoichiometry changes in the uppermost atomic layer. Using ARXPS for calibration TOF-SIMS has shown to be a suitable technique to control the oxide layer on GaAs wafer.

AS-TuP13 Surface Energy Change and Hydrophilic Formation of PE, PS and PTFE Films Modification by Hydrogen Ion Assisted Reaction*, **J. Cho**, K.H. Yoon,* Yonsei University, Korea*; S.K. Koh,* KIST, Korea

The Polyethylene (PE), Polystyrene (PS) and Polytetrafluoroetyhylene (PTFE) surface modification has been investigated by hydrogen ion assisted reaction with oxygen environment. The IAR is a kind of surface modification technique using ion beam irradiation with reactive gas environment. The hydrogen ion beam energy was 1 keV, ion dose were varied from 5ï,´1014 to 1ï,´1017 ions/cm2, and amount of oxygen blowing gas fixed 4 sccm (ml/min). Wettability was measured by water contact angles of water contact angle measurement, and the surface functionality was analyzed by x-ray photoelectron spectroscopy. The contact angle of water to PE modified by argon ion beam only decrease from 95 to 52 degrees, and surface energy was not changed significantly. But, the contact angle using hydrogen ion beam with 4 sccm oxygen environment was stiffly decreased to 8 degree and surface energy 65 ergs/cm. In case of PS, the contact angle and surface energy changes were similar results of PE, but the contact angle of PTFE samples decreased with ion dose up to 1ï,´1015 ions/cm2, increased at higher dose, and finally increased to the extent that no wetting was possible at 1ï,´1017 ions/cm2. The PTFE samples irradiated with argon with oxygen environment had lower contact angle than hydrogen with oxygen, even though the samples with oxygen environment

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[1] **ASSD Student Poster Competition Participant**

[2] **ASSD Student Poster Competition Participant**

developed hydrophilic groups on the irradiated surfaces. This results was due to the hydrogen ion beam that affect the surface cleaning for removing the impurities on PE surface and, then hydrogen ion beam was activated with C-H bonding to make some functional groups in order to react with the oxygen gases, finally, unstable PE surface can be changed from hydrophobic to hydrophilic formation such as C-O and C=O from the XPS analysis, and the ion assisted reaction is very effective tools to attach reactive ion species to form functional groups on C-C bond chains of PE.

AS-TuP14 Control of Intracellular Signal Transduction Using Self-Assembled Monolayers of Alkylthiolates on Gold*, **K.B. McClary**[1], D.G. Grainger,* Colorado State University

Self-assembled monolayers of terminally-functionalized alkylthiolates on gold have been used to interrogate cell-biomaterial surface interactions at the extracellular and intracellular level. The goal of this research is to provide molecular level information on the surface determinants necessary to produce predictable, controllable biological responses to implanted materials. Various aspects of "outside-in" communication between cells and material surfaces have been investigated. Formation of focal contacts and stress fibers, early indicators of effective intracellular signaling, was observed to be surface-chemistry dependent, and correlated with protein behavior on different surface chemistries. The primary cellular regulators of these events were examined using well-controlled alkylthiol surface chemistries. Activation states of the GTPase RhoA were determined and shown to be surface chemistry-dependent. RhoGDI levels and intracellular localization were also shown to be surface-chemistry dependent. Cells cultured on -CH3 terminated SAMs, which normally exhibit a low growth phenotype, were transfected with a constitutively active RhoA mutant. Transfected cells exhibited significant increases in cell length. However, no focal contact formation was observed. These results show that genetic alteration of intracellular regulators is incapable of overcoming the lack of extracellular stimuli, in the form of adsorbed ECM proteins, present on -CH3 terminated SAM surfaces. In summary, extracellular and intracellular information indicates that surface chemistry is capable of modulating communication between a cell and its extracellular environment. These data provide new, valuable molecular level information necessary to develop rational cause and effect relationships between a material's surface chemistry and biological response.

AS-TuP15 Core-level Satellites and Outer Core-level Multiplet Splitting In Mn Model Compounds*, **A.J. Nelson**, J.G. Reynolds,* Lawrence Livermore National Laboratory*; J.W. Roos,* Ethyl Petroleum Additives

We report a systematic study of the 2p, 3s and 3p core-level photoemission, satellite structures and valence bands of Mn model compounds. Charge-transfer from the ligand state to the 3d metal state is observed and is distinguished by the prominent shake-up satellite about 5 eV higher than the Mn 2p@sub 3/2@ peak for of all the Mn@super +2@ species and MnPO@sub 4@. The Mn 3s final state configuration can be either 3s3d@super 5@ or 3s3d@super 6@L depending on final state screening effects due to the ligand. We observe that the Mn 3s multiplet splitting becomes smaller as the Mn oxidation state increases, except for the Mn-phosphate species. Also, the 3s final state has @super 7@S and @super 5@S symmetry. In the @super 7@S state, the remaining 3s electron is well correlated with 3d electrons of parallel spin, while in the @super 5@S state the two spins are antiparallel. This electron correlation reduces the branching ratio of the @super 7@S:@super 5@S states as experimentally observed. In addition, as the ligand electronegativity decreases, the spin state purity is lost in the 3s spectra and the spectra becomes representative of mixed unscreened (3d@super N@) and locally screened (3d@super N+1@) final states. Our results are best understood in terms of configuration-interaction (CI) calculations including intrashell electron correlation, charge-transfer and final-state screening.

AS-TuP16 Optimizing Signal Intensities in REELM and SAM Microscopies: A Comparision of Instruments Operated in Fixed-Analyzer-Transmission (FAT) and Fixed-Retard-Ratio (FRR) Modes*, **E. Paparazzo**, L. Moretto,* Consiglio Nazionale delle Ricerche, Italy*; S.A. Lea, D.R. Baer,* Pacific Northwest National Laboratory

Signal intensity is the main factor for chemical contrast in reflected electron energy loss microscopy (REELM) and scanning Auger microscopy (SAM) images of surfaces. We report here on REELM and SAM signal intensities measured as a function of the primary beam energy (Ep) for two Auger microprobes: one operated in the fixed analyzer transmission (FAT) mode (Cameca 'Nanoscan 50', Rome), the other in the fixed retard ratio (FRR) mode (PHI '680 Auger Nanoprobe', Richland). The aim of this work is to quantitatively determine the extent to which each type of microprobe affects the relative intensities of REELM and SAM signals. To accomplish this task we conducted a comparative analysis in the two laboratories using atomically-clean Al metal as a sample. We measured the intensity ratio between the first bulk plasmon signal and the Auger Al LVV signal (KE ~ 70 eV) as a function of Ep, which was chosen at several values within the range 200-2000 eV. We found that for both the FAT and FRR microprobe this ratio decreases by a factor ~ 10 upon increasing Ep from 200 to 2000 eV. These findings are discussed in light of both the energy resolution and response function associated with the FAT and FRR operation modes in the KE range considered, and they are used to account for the chemical contrast of REELM and SAM images acquired in the two microprobes at differing Ep's. We show that our work can help devise an optimal compromise between chemical contrast, surface-specificity and chemical speciation in both REELM and SAM imaging, whether the two methods are performed in FAT or FRR Auger microprobes.

AS-TuP17 The Develpment and Application of a High Speed Etching Source for Destructive Depth Profiling*, **A.J. Roberts**, C.J. Blomfield, S.C. Page, D.J. Surman,* Kratos Analytical, UK

The development and application of a low energy argon ion beam source for destructive depth profiling, combined with X-ray photoelectron spectroscopy (XPS) are presented. This compact Kaufman ion source which combines extremely high sputter rates and low ion beam acceleration potentials, reduces ion induced mixing of the surface atoms. The properties of this ion source mean that concentration depth profiling through several hundred nanometer thick layers is possible, whilst retaining good interface resolution. Rotation of samples during sputter profiling is shown to improve interface resolution. The depth profiling capabilities of this high speed etching source will be demonstrated through a number of challenging samples. Atomic concentration profiles through a three layer sample have been performed as a function of ion acceleration voltages, and the effect on interface resolution is discussed. A further example of depth profiling through an inorganic material with a thin metal underlayer on polyester is shown. Chemical state information is retained from the inorganic oxide layer, with some reduction of the oxide layer observed due to the preferential sputtering of oxygen from the surface during profiling. Data presented shows no decrease in the sputter rate due to positive charging of electrically insulating samples during the sputtering process.

AS-TuP18 A Dual Anode Monochromatic X-ray Source*, **S.C. Page**, C.J. Blomfield, B.J. Tielsch, D.J. Surman,* Kratos Analytical, UK

High energy Ag L@alpha@ X-rays have several advantages over the more commonly employed Al K@alpha@ source. A photon energy of 2984.3eV means that a Ag source can generate higher energy core levels, Auger series and has a greater excitation volume. A further advantage over other high energy sources is that the Bragg condition may be satisfied via a second order diffraction within the confines of the conventional Al K@alpha@ monochromator body with only minor modifications. We have now for the first time implemented a Ag monochromator as a modification to the standard Al monochromator on a modern magnetic lens based electron spectrometer, the Axis Ultra. The anode of the Al monochromator has been adapted to have both a conventional Al face as well as an additional Ag face, thus changes between source may be made by minor adjustment without breaking vacuum. The great improvement gained in photoelectron collection efficiency by employing magnetic lens technology improves the sensitivity and ultimate usability of the Ag source making it a viable alternative for the measurement of deep 1s core levels and Auger parameters. The results presented show the performance of the Ag source to give resolution better than 0.9 eV FWHM on Ag and a sensitivity greater than 4,300 CPS on Au at a resolution of 1.3eV. Further results highlighting the usefulness of the source on practical samples will be presented.

AS-TuP19 Scanning Tunneling Microscopy and X-ray Photolectron Spectroscopy Studies of WO3 Thin Films Submitted to Various Thermal Treatments in Air and Ultra High Vacuum*, **S. Santucci**, L. Lozzi, M. Passacantando,* University of L'Aquila and INFM, Italy*; L. Ottaviano,* INFM, Italy*; C. Cantalini, L. Odorisio,* University of L'Aquila, Italy

The gas sensitive properties of WO3 thin films seem to be due to a loss of oxygen at the surface, which determines the presence of active sites for the reaction with gases (Co,NOx,ozone). The reactivity of the WO3 films is strongly influenced by the morphology and surface properties. In this work the surface electronic and structural properties of about 150 nm thick WO3 films, deposited in high vacuum by thermal evaporation onto Si substrates, have been studied in UHV by means of XPS and Scanning Tunneling

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[1] **ASSD Student Poster Competition Participant**

Microscopy/Spectroscopy (STM/STS). After the deposition these films have been annealed in atmospheric owen for 24 h at different temperatures (300 and 500° C) to stabilise the film morphology. The XPS measurements, by using a monochromatic Al source to follow W 4f, O 1s peaks and the valence band, have been performed on these samples both as prepared and after a re-annealing in UHV at temperatures ranging from 50 to 600 ° C, . The UHV re-annealing procedure strongly modifies the W 4f peak of both the as deposited and 300 ° C samples, showing the loss of oxygen. Moreover, at the Fermi edge, before the UHV annealing there is a small signal due to the presence of metallic states. This signal after the UHV annealing strongly increases, indicating the presence of an high density of states at the Fermi edge. Instead the 500 ° C sample, after the heating in UHV has shown a substantial stability of the nearly stoichiometric WO3 phase. Using STM in UHV we have investigated the morphology of the samples at room temperature and while scanning at elevated temperatures up to 600 °C. In particular we have simoultaneously taken I-V curves at the boundaries and centers of the typical grains of the polycrystalline sample. Our findings on the electronic structure of the samples close to the Fermi level are in agreement and allow clearer understanding of the findings from a parallel XPS study.

AS-TuP20 Radiation Damage Study of n-Alkanethiols Deposited on Platinum*, **N. Franco**, T. Van Buuren, C. Bostedt, L.J. Terminello,* Lawrence Livermore National Laboratory

The potential technological applications of Self Assembled Monolayers (SAM's) has increased dramatically in the past few years. Most of these applications exploit the flexibility and simplicity of the monolayer film growth. Alkanethiols adsorbed on nobel metals are perhaps the best example of theses ordered interfaces and, in these cases, it has been shown that the stability of the adsorbed molecules is strongly related with the dimension of the carbon chain. We performed valence band and core level synchrotron radiation spectroscopy studies of different n-alkanethiols adsorbed on platinum in order to investigate the stability of these films under a Ultra Violet (UV) or soft X-ray exposure. Additionally we measured the change in the empty states by X-ray Absorption Spectroscopy (XAS) and we imaged the surface by Atomic Force Microscopy (AFM) to determine surface morphology. We will present results that suggest a change in the structure of the molecules adsorbed caused by irradiation. This change is related to the photon flux and is not energy dependent. @FootnoteText@ C. Bostedt is supported by the German Academic Exchange Service DAAD, N. Franco by the Spanish education and culture office. The work is supported by the US-DOE, OBES Material Sciences under contract W-7405-ENG-48, LLNL.

AS-TuP21 Surface-initiated Anionic Polymerization: Investigation of Functionalized Surfaces and In-situ Polymer Films*, R.C. Advincula,* University of Alabama at Birmingham, US*; Y. Nakamura, S. Inaoka, Q. Zhou, **J. Mays**,* University of Alabama at Birmingham

The surface initiated anionic polymerization is a "grafting from " approach to tethering polymer chains to surfaces. Although various surface-initiated polymerization schemes have appeared recently, we seek to utilize the anionic polymerization approach with its potential to forming monodispersed polymers of controlled MW through "living" polymerization. In this report, we describe the synthesis of the initiator; diphenylethylene (DPE) silane derivative, the activation towards initiation, polymerization mechanism, and characterization of the polymers bound on the substrate. An important focus is the analysis of the substrate before and after formation of the self-assembled-monolayer (SAM) of the initiator. We have utilized electrochemical methods, contact angle, quartz crystal microbalance (QCM), ellipsometry, atomic force microscopy (AFM), and surface plasmon resonance spectroscopy (SPS) to characterize the surfaces. We then correlated the initiation and the polymerization mechanism with the properties of the functionalized substrate. In particular we were interested in observing the density and distribution of the initiating species on the surface in a mixed system (alkylsilane) We have observed a dependence on the domain size and mixture composition of the initiator to the microstructure and physical properties of the resulting polymer (polystyrene and PMMA) films. Further characterization will be done on the polymer films by scale-up (using silica particles) and detachment from the surface.

AS-TuP22 Surface Limiting Factors of the Growth of Metallic Nanoparticles*, **R. Tannenbaum**,* Georgia Institute of Technology*; H. Rotstein, A. Novick-Cohen,* Technion-Israel Institute of Technology, Israel

Chemical synthesis of metal clusters, unlike UHV methods, offers a great deal of flexibility in manipulating cluster properties, such as the oxidation state and the reactivity of the metal clusters due to particle size variations, all within the bounds of the nanoscale regime. Stabilization and control of the size of metallic colloidal particles are achieved in polymer solutions, due to the adsorption of the polymer to the coagulating metal fragments, to form a layer which separates the particles sufficiently in order to keep van der Waals forces below thermal energy levels. Among the most promising chemical avenues, is the thermal decomposition of metal carbonyls in the presence of polymers with relatively low reactivity (e.g. polystyrene) under controlled inert atmosphere, resulting in the formation of zero-valent metallic particles. During the decomposition reaction of the metal carbonyl precursors highly reactive intermediates are formed, resulting in two major subsequent reaction pathways: (a) Aggregation to form small clusters; and (b) Interaction with the polymer. The final particle size and particle size distribution will be a direct function of the various facets of this complex mechanism. For the growth of zero-valent cobalt clusters, there is an inverse correlation between cobalt cluster particle size and the polystyrene concentration in the reaction solution. The increase in the concentration of polystyrene in solution will result in an increase of the concentration of the adsorbed polystyrene layer, and hence a decrease in the final cobalt cluster size. The thickness of the adsorbed polymer layer is calculated by using a combination of TEM and STM measurements. The difference in the particle size diameters calculated by the two methods provide an indication of the thickness of the polymer layer. We will present working models for the correlation between the final cobalt nanocluster size and the extent of metal-polymer surface interactions.

AS-TuP23 Time-Resolved Observations of Failure along Polymer-Glass Interfaces in Humid Environments@footnote 1@*, **J.T. Dickinson**, N.Z. Hertelendy, S.C. Langford,* Washington State University

Adhesive interfaces play a critical role in microelectronic packaging, as well as in aerospace, automotive, and civil structures. The accelerated failure of strained adhesive bonds due to moisture is of considerable interest. By studying very small bonded zones (area @<=@ 1 mm@super 2@) one greatly enhances the influence of environmental attack, allowing for accelerated testing. To measure failure kinetics, we compare videotaped micrographic records of failure along ethylene vinyl acetate/soda lime glass interfaces in humid atmospheres with simultaneously acquired measurements of applied force. The interface is viewed through the glass substrate with an optical microscope. With increasing applied stress and relative humidity, the time required to produce an observable defect and the total time to failure decrease in a monotonic fashion. With increasing stress, the size of the crack at the onset of unstable critical crack growth also decreases. Visible crack growth prior to unstable failure is rate limited by the diffusion of water to the crack tip. The time required to produce a visible defect can be accounted for on the basis of chemically assisted failure, where the crack velocity depends directly on the change in surface energy due to water sorption (not transport limited). A quantitative model for the dependence of failure on stress and humidity is presented. @FootnoteText@ @footnote 1@This work is supported by the NSF Surface Engineering and Tribology Program under Grant CMS-98-00230.

Applied Surface Science Division
Room 6A - Session AS-WeM
Gaede-Langmuir Award Address and Quantitative Surface Analysis

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

8:20am **AS-WeM1 Monte Carlo Simulations for Tilted Electron Multipliers@footnote 1@**, ***Y.S. Choi***, *S.G. Yu, J.M. Kim,* Samsung Advanced Institute of Technology, Korea

Microchannel electron multipliers are simulated using the Monte Carlo method. Gains of secondary electrons are calculated for different structures of the electron multiplier. For a tilted cylindrical channel of the electron multiplier the gain has a maximum at a tilt angle. The maximum gain is about a thousand times larger than that of the not-tilted channel. An explanation is suggested for the improvement of gain in the tilted channel. @FootnoteText@ @footnote 1@This work was supported by the Korean Ministry of Science and Technology through the Creative Research Initiative program.

8:40am **AS-WeM2 Gaede-Langmuir Award Address: Early Development of Auger and ESCA Instrumention***, **P.W. Palmberg**,* Physical Electronics **INVITED**

The role of the author in the early development of practical Auger and ESCA instrumentation is reviewed. The significance of these early 1970's developments to the surface science community and industrial users is discussed. The authors contributions to both instrument and application development are outlined.

9:40am **AS-WeM5 Consistent, Combined Quantitative AES and XPS Digital Data Bases - Convergence of Theory and Experiment***, **M.P. Seah**, I.S. Gilmore, S.J. Spencer,* National Physical Laboratory, United Kingdom

AES and XPS have more aspects in common than they have in distinction. Therefore, tests of aspects for one spectroscopy, applicable to the other, should be validated for both. Digital databases for elemental spectra for both AES and XPS have thus been measured using an electron spectrometer that has fully calibrated intensity and energy axes. This provides true spectra to give absolute Auger electron yields and relative photoelectron yields. The AES database is measured for both 5 and 10 keV electron beam energies, whereas the XPS database is measured for both Al and Mg unmonochromated X-rays at the magic angle. The combination of these databases allows a refinement of the theories to obtain an overall convergence between theory and experiment. Improvements have been obtained by identifying three classes of parameter to consider: (i) parameters for both AES and XPS, such as electron transport, the methodology of evaluation of peak areas and the spectrometer response function, (ii) parameters for AES only, such as the electron ionisation cross section, backscattering and specific electron backgrounds and (iii) parameters for XPS only, such as the photon-ionisation cross section. Using this approach, improvements to the theories of all three classes of parameter and their method of use have been established. The formalism for quantitative analysis in AES and XPS, using relative sensitivity factors, has been revised to develop an accurate matrix-less formalism that is very simple for use by the analyst. This formalism has the same accuracy as the full matrix formalism but its simplicity permits ready extension to systems beyond binary. Details of these and recent advances, particularly with improvements in the background subtraction for the peak area measurement, lead to excellent convergence between theory and the data. This will be discussed, together with outstanding issues for general quantitative analysis with AES and XPS.

10:00am **AS-WeM6 Relationships between Parameters Describing Inelastic Electron Scattering in Solids***, A. Jablonski,* Polish Academy of Sciences*; **C.J. Powell**,* National Institute of Standards and Technology

The terms inelastic mean free path (IMFP), effective attenuation length (EAL), and mean escape depth (MED) are frequently used to specify the surface sensitivity of AES and XPS and also for quantitative applications. These terms are different conceptually because of the effects of elastic-electron scattering, and generally have different numerical values. In addition, EAL and MED values depend on the instrumental configuration. We apply an analytical formalism developed from a solution of the kinetic Boltzmann equation within the transport approximation@footnote 1@ to demonstrate the relationships between the IMFP, EAL, and MED for selected elemental solids and for common measurement conditions. It is shown that EAL and MED values can be derived from an analytical representation of the emission depth distribution function and values of the IMFP and the transport mean free path.@footnote 2@ Examples are given to show the magnitude of elastic-scattering effects on MED values for angle-resolved XPS and AES. If XPS or AES data are acquired for emission angles between zero and 60°, the ratio of the MED to that found with elastic scattering neglected is approximately constant (to within 10 %), and this ratio can be used to determine an average value for the EAL. This EAL value can then be used to establish the depth scale in the data analysis. For emission angles greater than 60°, conventional data analysis (in which elastic-scattering effects are neglected) becomes unreliable. Finally, we show ratios of the EAL to the IMFP for XPS from the Au 4s subshell with Mg K@alpha@ x rays as a function of emission angle and depth; this ratio has a weak dependence on emission angle from zero to 40° but a more pronounced dependence for larger emission angles. @FootnoteText@ @footnote 1@I. S. Tilinin, A. Jablonski, J. Zemek and S. Hucek, J. Electron Spectrosc. 87, 127 (1997). @footnote 2@A. Jablonski and C. J. Powell, J. Electron Spectrosc. (in press).

10:20am **AS-WeM7 Straightforward Methods for Accurate Estimation of Attenuation Length and Similar Quantities in XPS and AES***, **P.J. Cumpson**,* National Physical Laboratory, UK*; M.P. Seah, I.S. Gilmore,* National Physical Laboratory, UK, United Kingdom

The surface-sensitivity of X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) is due to strong inelastic scattering of electrons. Elastic scattering also takes place, and modifies@footnote 1@ the absolute intensities, the sensitivity factors, the intensities from layers, and (in the case of XPS) the asymmetry parameter @beta@, all of which feed-in to quantitative analysis of spectra. The modification is a multiplicative factor of between 3% and 30% depending on the kinetic energy and material. The behaviour of the asymmetry parameter is particularly important for those using monochromated XPS instruments. Elastic scattering affects these quantities in a straightforward way. This leads to some simple recommendations on analysis geometry, and estimation of Attenuation Lengths to optimise the accuracy of quantifications without increasing complexity. One can measure surface composition and layer thicknesses to known, acceptable accuracy,@footnote 2@ provided one can estimate the Attenuation Length of signal electrons in the sample being analysed. In particular, Attenuation Lengths for organic materials are important in defining polymer, lubricant or contamination surface layers by Angle-Resolved XPS. We therefore pay particular attention to how to estimate Attenuation Length values for an arbitrary organic material. These estimates are in excellent agreement with Monte Carlo calculations. @FootnoteText@ @footnote 1@ A Jablonski, Surf. Sci. 364 (1996) 380. @footnote 2@ P J Cumpson and M P Seah, Surf. Interface Anal. 25 (1997) 430.

10:40am **AS-WeM8 Quantitative Auger Spectroscopy: Applications to Process Development and Qualification of Tungsten Silicide Films***, **C.T. Dziobkowski**, S.C. Ramac,* IBM Corp., E. Fishkill*; E.D. Adams,* IBM Corp., Burlington

Tungsten silicide films are widely used in gate conductors for DRAM gate structures for complementary metal-oxide-silicon (CMOS) integrated circuits. Careful characterization of these films with Rutherford backscattering spectrometry (RBS) and Auger electron spectroscopy (AES), the two most commonly used techniques, helps define and control a practical tungsten silicide process. The correct choice of analytical parameters is essential in obtaining accurate and reproducible compositional analysis. The enhanced depth resolution of Auger spectroscopy is especially critical in viewing the region of the interface between the tungsten silicide and polysilicon. Currently, an intrinsic polysilicon cap is used between the doped polysilicon and the CVD deposited tungsten silicide to prevent an unwanted secondary reaction between phosphorus and tungsten hexafluoride which leads to a tungsten enriched interface. This enriched tungsten interface can result in abnormal oxidation, stress and loss of adhesion between the intrinsic polysilicon and tungsten silicide. AES and RBS analytical techniques have been applied to examining the control of this interface to allow extension of CVD tungsten silicide to the thinner gate polysilicon needed for advanced technologies. Examples will be given of the effects of varied gate cap thickness of both amorphous and intrinsic polycrystalline silicon on the tungsten silicide / polysilicon interface using these analytical techniques. The interface composition is known to have a profound effect on the performance of these devices.

11:00am **AS-WeM9 Naphthalocyanine Molecules onto Si(111)7x7 and Si(100)2x1: Modes of Adsorption and Effects of Oxygen Doping Investigated with XPS***, L. Ottaviano,* INFM, Italy*; **L. Lozzi**, A. Montefusco, S. Santucci,* University of L'Aquila and INFM, Italy

We have deposited in ultra high vacuum various thickness of metal free naphthalocyanine (H@sub 2@NPc) onto Si(111)7x7 and Si(100)2x1 and studied in situ the interfaces by means of standard monochromatized X-ray Photoelectron Spectroscopy.@footnote 1@,@footnote 2@ By comparing the core level N1s and C1s spectra obtained for the pure molecule with those typical of the interface at submonolayer and intermediate level of deposition we derived information on the ways of adsorption of the isolated molecules onto the substrates used. In particular NPc adsorbs planarly to the Si(111)7x7 substrate showing strong chemisorption effects involving all the atoms of the molecule. On the other hand, the chemisorption involves only two C atoms when using the Si(100)2x1 substrate. In this case the NPc molecules are likely to be adsorbed in a out of planar mode. In a dedicated series of experiments, the interfaces have been doped with oxygen. An integer ratio of the estimated oxygen atoms per Naphthalocyanine (NPc) molecule in the quantitative XPS elemental analysis of the spectra gives evidence for a preferential adsorption of oxygen in molecular form onto NPc. A careful analysis of the spectra indicates that oxygen mainly interacts with the inner porphyrin structure of the molecule. @FootnoteText@ @footnote 1@ L. Ottaviano, L. Lozzi, and S. Santucci, Surf. Sci. (in press). @footnote 2@ L. Ottaviano, L. Lozzi, A. Montefusco, and S. Santucci, Surf. Sci. (submitted).

11:20am **AS-WeM10 Technique for Production of Calibrated Metal Hydride Films***, **R.A. Langley**, J.F. Browning, S.D. Balsley, J.C. Banks, B.L. Doyle, W.R. Wampler,* Sandia National Laboratories

A technique has been developed for producing calibrated metal hydride films for use in the measurement of high-energy (5-15 MeV) particle reaction cross sections for hydrogen and helium isotopes on hydrogen isotopes. Absolute concentrations of various hydrogen isotopes in the film is expected to be determined to better than ± 2% leading to the capacity of accurately measuring various reaction cross sections. Hydrogen isotope concentrations from near 100% to 5% can be made accurately and reproducibly. This is accomplished with the use of high accuracy pressure measurements coupled with high accuracy mass spectrometric measurements of each constituent partial pressure of the gas mixture during loading of the metal occluder films. Various techniques are used to verify the amount of metal present as well as the amount of hydrogen isotopes: high energy ion scattering analysis, PV measurements before, during and after loading, and thermal desorption/mass spectrometry measurements. The most appropriate metal to use for the occluder film appears to be titanium but other occluder metals are also being considered. Calibrated gas ratio samples, previously prepared, are used for the loading gas. Deviations from this calibrated gas ratio are measured using mass spectrometry during and after the loading process. These techniques will be discussed and results presented.

11:40am **AS-WeM11 The Role of SIMS for Interface Control in the MBE Growth of InGaSb/InAS Strained Layer Superlattices***, **J.S. Solomon**, M.L. Seaford, D.H. Tomich, K.G. Eyink,* Air Force Research Laboratory

Secondary ion mass spectrometry (SIMS) was used to evaluate beam flux control used for the molecular beam epitaxial (MBE) growth of an indium gallium antimonide/indium arsenide (InGaSb/InAs) strained layer superlattice. Two methods of control were compared: (1) a computer controlled mechanical shutter and (2) a computer controlled system consisting of both a mechanical shutter and a servo operated valve. The issue is the unintentional incorporation of arsenic in the InGaSb layer due to inadequacies of beam flux control mechanisms, such as shutters, to completely shield sources that are part of a cyclic growth process. Test structures of GaAs and GaSb were used in the study with the former used to evaluated antimony control and the latter used to evaluate arsenic control. SIMS results showed arsenic levels as high as 2-4% in GaSb layers when only a mechanical shutter was used. Neither arsenic nor antimony were detected in their respective test structures when growth was controlled with the combination of mechanical shutter and valve. SIMS results correlated with arsenic and antimony levels determined by high resolution x-ray diffraction (HRXRD) analysis of the same test structures. Finally, HRXRD showed improved interface integrity in the SLS structures grown using the combination of mechanical shutter and vale to control arsenic and antimony beam fluxes.

Surface Science Division
Room 607 - Session SS2+AS+PS-WeM

Ion-Surface Interactions I

Moderator: L. Hanley, University of Illinois, Chicago

8:20am **SS2+AS+PS-WeM1 Trapping and Desorption of Energetic Cu Atoms on Cu(111) and (001)Surfaces at Grazing Incidence***, **D.E. Hanson**, A.F. Voter, J.D. Kress,* Los Alamos National Laboratory*; X.-Y. Liu,* Motorola, Inc.

Cu is widely used as an interconnect in semiconductor chips. It is deposited by ionized physical vapor deposition on sub-micron features that have sidewalls nearly parallel to the incident ion beam. Molecular dynamics (MD) simulations have shown that, for angles of incidence (with respect to normal) up to 20 degrees, the sticking probability is unity for all energies; the impact atom penetrates and loses all of its kinetic energy to the surface. As the impact angle increases, the probability for the impact atom to reflect increases, reducing the sticking probability. Surprisingly, for angles above 70 degrees, the sticking probability increases with impact angle. We have performed MD simulations of Cu atoms impacting both Cu(111) and (001) surfaces at grazing incidence and find that this unexpected increase in sticking probability is a consequence of trapping (or surface skipping). An energetic Cu atom (10 ¾ E ¾ 100 eV) can become trapped by the mean attractive potential above the surface, oscillating normal to the surface. While in this trapped state, it can traverse hundreds of Å as it dissipates energy to the surface. Until the atom either desorbs or comes to rest, it experiences an average energy loss rate that is piecewise linear, typically comprised of two or more roughly linear (dE/dt = constant) regions. The process can be characterized by two parameters: the desorption probability at each oscillation and an average energy loss rate (per oscillation) that is independent of energy. These parameter values are the same for both the (111) and (001) surfaces. A phenomenological model based on these parameters is presented, and the predictions of sticking probability, average energy transfer to the surface, and total distance traveled along the surface, agree with full MD simulations. The dependence of the desorption probability on the surface temperature, was also studied.

8:40am **SS2+AS+PS-WeM2 Dynamics of NO@super +@ Abstraction of Oxygen on Al(111)***, **M. Maazouz**, P.L. Maazouz, D.C. Jacobs,* University of Notre Dame

Energetic collisions between molecules and surfaces can activate a number of reaction processes, such as electron transfer, activated dissociative chemisorption, dissociative scattering, atom abstraction, and sputtering. The branching into each of these channels can be affected by the initial internal energy (electronic, vibrational, and rotational) and collision energy of the molecule. Reactive collisions of NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v=1) with oxygen-covered Al(111) are explored across a range of hyperthermal energies (5-80 eV). A laser forms the incident ions from the neutral NO via resonance-enhanced multiphoton ionization (REMPI). This produces NO@super +@(@Chi@ @super 1@@Sigma@@super +@, v) in a selected vibrational level (v=0-6) of the ground electronic state. Scattered products include O@super -@, NO@super -@, and NO@sub 2@@super -@. The latter product arises from an atom abstraction channel and is the main focus for the present study. The NO@sub 2@@super -@ formation shows a strong dependence on the oxygen coverage and the NO@super +@ primary energy. Detailed reaction mechanisms leading to NO@sub 2@@super-@ emergence will be discussed.

9:00am **SS2+AS+PS-WeM3 Oxygen Negative Ion Emission from Al(100) Bombarded by Li@super+@ Ions***, **J.A. Yarmoff**, W.K. Wang, B.-L. Young, B.C. Corbitt,* University of California, Riverside*; Z. Sroubek,* Academy of Sciences of Czech Republic

The intensity of oxygen negative ions sputtered from metal surfaces (V, Mo, Cu) by rare gas ions is known to increase by up to 3 orders of magnitude when the surface work function is lowered by alkali metal adsorption. A resonant charge transfer process from the surface bands to the oxygen affinity level is apparently responsible for the negative ion formation, and such a process is strongly dependent on the surface potential. We have measured the intensities and kinetic energy distributions of O@super-@ sputtered from Al(100) via bombardment by 200 eV Li@super+@ ions. In contrast to experiments with rare gas ions, the O@super-@ intensity is found to be relatively independent of the work function changes induced by Cs deposition (@DELTA@@phi@ = - 3 eV). For O@super-@ kinetic energies above 20 eV there is no increase in the yield, and it increases by only a factor of 2-3 at lower O@super-@ kinetic energies. The energy distribution depends exponentially upon the O@super-@ kinetic energy, and has a cutoff at about 120 eV. These results suggest that the yield of oxygen particles sputtered from clean Al(100) by Li@super+@ is already nearly completely ionized due to the local potential perturbation caused by the projectile. Thus, a further lowering of the surface potential by the deposition of alkali adsorbates has little effect. This is clear evidence of the localized nature of the resonant charge exchange process, and the first evidence that such a local effect can be induced by the primary particle.

9:20am **SS2+AS+PS-WeM4 Matrix Dependent He+ Neutralization by Adsorbates: An ISS Study of S and Cl on TiO@sub 2@(110)***, **W. Hebenstreit**, E.L.D. Hebenstreit, U. Diebold,* Tulane University

We have studied the adsorption of S and Cl on TiO@sub 2@(110) with low-energy He@super +@ ion scattering spectroscopy (ISS) , X-ray photoelectron spectroscopy (XPS), and scanning tunneling microscopy (STM). Because of its high surface sensitivity, ISS is ideally suited to determine the chemical composition of surfaces. While it is well known that quantification of ISS spectra is influenced by trajectory-dependent blocking, the element-specific neutralization of the probing ion is generally assumed not to be matrix dependent. We found that the neutralization of He+ ions (400 - 2450 eV, scattering angle 139°) scattered on Cl or S (adsorbed on TiO@sub 2@(110)), depends strongly on sample pretreatment and adsorption site. Cl (~ 1 ML) and S (~ 2/3 ML) give rise to pronounced peaks in ISS spectra when adsorbed on the sputtered TiO2 sample (1 keV Ar@super +@, flux 1.5 10@super 16@ cm@super -2@), but both species cannot be detected after adsorption at RT on the annealed, stoichiometric TiO@sub 2@(110) surface (coverage ~ 1/3 ML). STM shows that the adsorbates are located on the rows of 5-fold coordinated Ti atoms. When dosed at 573 K, S adsorbs at the position of bridging oxygen atoms, where it forms a (1x3) superstructure. In this case S becomes "visible" again for ISS. All spectra (on sputtered and annealed substrates) show a decrease in the O and Ti ISS signal due to blocking induced by the adsorbates. Subsurface positions of the adsorbates in the "invisible cases" can be excluded by STM. The difference in neutralization is due to different electronic structures of the substrate surface: (a) semiconducting with a 3 eV band gap when annealed; (b) metallic due to defect states and oxygen deficiency after sputtering. In case of S located at the position of bridging oxygens, neutralization is affected by the different local bonding.

9:40am **SS2+AS+PS-WeM5 Hyperhhermal Ion - Surface Interactions***, **J.W. Rabalais**,* University of Houston **INVITED**

The chemical and physical phenomena accessible by means of low energy ion beams on surfaces will be discussed. Such energetic reactive ions can stimulate selected physical and chemical processes, such as film deposition, growth, synthesis, and shallow implantation within a nonequilibrium UHV environment. The 'low energy' or 'hyperthermal' range is considered to be 5 eV to a few keV. The lower limit is of the order of chemical bond energies. In this limit, chemical bonding interactions become significant, the binary-collision approximation (BCA) becomes questionable, and inelastic interactions can alter the ion trajectories. In the high energy limit, the sputtering yield becomes equivalent to or higher than the beam flux, classical ion trajectory simulations using the BCA provide a satisfactory description of the collision events, and the impinging ions are implanted in the subsurface layers. Mass-selected ion beam deposition (IBD) allows independent control over parameters such as ion energy and type, ion fluence and dose, substrate temperature, and background gases. The advantages of IBD for stimulation of chemical reactions, control of film stoichiometry, low temperature epitaxy, good film-substrate adhesion, and for growth of materials with metastable structures, isotopic purity, and high densities will be contrasted with the disadvantages, such as production of defects, imperfections, and amorphous materials and the limited thicknesses of IBD films. Examples of the use of mass- and energy-selected beams for hyperthermal surface reactions, film growth, synergism between ion energy and substrate temperature, and shallow implantation will include: Si+ ion homoepitaxy, the growth SiO2 from pulsed Si+ and O+ beams, low energy Ti+ beams for growth of titanium silicide on silicon and mixed Ti-Al oxides on sapphire (a-Al2O3), growth of diamond-like carbon, growth of Ag(111) on a Ni(100) surface, and survival probabilities of scattered TiClx cluster ions.

10:20am **SS2+AS+PS-WeM7 Dissociation and Energy Distribution Processes in XY@super -@(CO@sub 2@)@sub n@ (XY = ICl, I@sub 2@, and Br@sub 2@) Collision onto Silicon Surface***, **S. Koizumi**,* Genesis Research Institute, Inc., Japan*; H. Yasumatsu, A. Terasaki, T. Kondow,* Toyota Technological Institute, Japan

Collisional dissociation induced by impact of a cluster anion, ICl@sup -@(CO@sub 2@)@sub n@ (n = 0 - 20), onto a silicon surface were studied by measuring the branching fractions of the ICl@sup -@ dissociation and the translational energies of the product anions as functions of n and the collision energy (per ICl@sup -@) of ICl@sup -@(CO@sub 2@)@sub n@ in an apparatus consisting of a tandem time-of-flight mass spectrometer. It was found that the branching fraction of the ICl@sup -@ dissociation did not change with n at the collision energies of 30 - 70 eV. Molecular dynamics simulation showed that the impinging core ion, ICl@sup -@, tends to orient with the molecular axis of the core ion being at the angle of 55 ° with respect to the surface normal, whereas in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ (X = Br, I) collision, the molecular axis of the X@sub 2@@sup -@ core ion being in parallel to the surface plane. This finding together with prominent wedge effect in the X@sub 2@@sup -@(CO@sub 2@)@sub n@ collision leads us to conclude that the CO@sub 2@ molecules do not work as 'wedge' in the ICl@sup -@(CO@sub 2@)@sub n@ collision because of the unfavorable orientation of the incoming cluster anion. No discernible cage effect could also be related to the orientation. The translational energies of the product anions were interpreted in terms of energy redistribution of the collision energy among the degrees of freedom of the cluster anion and the surface atoms involved in the collision. It was also found that the I and Cl product ions reach quasi-equilibrium with the surface from the measurement of these translational energy distributions.

10:40am **SS2+AS+PS-WeM8 Angle Resolved Measurements of Ions and Neutrals Scattered from HOPG Surfaces upon Hyperthermal Glancing Incidence Irradiation with Large Polyatomic Ions: Charge Changing and Impact Orientation Phenomena***, M. Hillenkamp, J. Pfister, **M. Kappes**,* University of Karlsruhe, Germany*; R. Webb,* University of Surrey, United Kingdom

We have scattered a series of polyaromatic hydrocarbons and various fullerenes from graphite at hyperthermal kinetic energies (100-5000eV) under glancing incidence (75 degrees with respect to the surface normal). Resulting cations, anions and fast neutrals have been studied with a secondary time-of-flight mass spectrometer/detector rotatable about the scattering plane. The corresponding angular distributions have been compared to those obtained upon irradiation of HOPG with He@super +@ and Xe@super +@ ion beams under otherwise identical conditions. Molecular projectiles were typically studied as either singly or multiply charged parent cations. In addition to dominant neutralization, we also observe the scattering of smaller amounts of both cations and anions (parents and fragments). We discuss the relative yields of charge states in terms of charge transfer rate theories as well as in terms of postcollision decay processes (e.g. delayed electron loss). In comparing the surprisingly narrow (and near Gaussian) angular distributions determined for fast neutrals from fullerene scattering with those recorded for xenon, we find that while Xe is specularly scattered over the full energy range studied, fullerenes are scattered subspecularly - with the deviation from specular angle increasing with increasing collision energy. Molecular dynamics simulations with Brenner potentials suggest that this effect results from a combination of the comparatively long (>300 fesec) "turnaround " time of the molecular projectile and a significant perpendicular deformation of the layered target on the collision time scale. For the topologically much more anisotropic polyaromatic hydrocarbon projectiles we find structured fast neutral angular distributions suggestive of a simple dependence between impact orientation and scattering angle

11:00am **SS2+AS+PS-WeM9 Surface Structure Determination by Angle-Resolved Mass Spectroscopy of Recoiled Ions***, **G.S. Herman**,* Pacific Northwest National Laboratory

Low energy ion scattering (LEIS) and direct recoil spectroscopy (DRS) are powerful techniques for the determination of surface composition and structure. The combination of time-of-flight methods with an electrostatic time focussing analyzer has recently resulted in a new technique - mass-spectroscopy of recoiled ions (MSRI).@footnote 1@ The MSRI technique has an advantage over LEIS and DRS in that it has much higher mass-resolution and sensitivities. Results related to the exchange of @super 18@O into samples will be presented to illustrate the high mass-resolution. Furthermore, recent results indicate that in the angle-resolved mode, structural determinations can be performed. Angle-resolved MSRI (AR-

MSRI) results will be presented for CeO@sub 2@(001) and TiO@sub 2@(001)-Anatase films grown on SrTiO@sub 3@(001) substrates by molecular beam epitaxy and chemical vapor deposition, respectively. The experimental data are fit to calculations using the scattering and recoiling imaging code based on the binary collision approximation.@footnote 2@ The ideal CeO@sub 2@(001) surface is polar and predicted to be unstable. However, LEED results indicate that a sharp (1x1) pattern can be obtained. The structural model determined by AR-MSRI consists of an oxygen-terminated surface with a half monolayer of oxygen removed. This structure is consistent with a model based on the reduction of the surface dipole moment. The TiO@sub 2@(001)-Anatase surface has only recently been experimentally investigated in much detail. LEED measurements indicate that the surface undergoes a (1x4) reconstruction after a sputter and anneal cycle. A comparison between experiment and theory for several models for this reconstruction will be presented. @FootnoteText@ @footnote 1@ K. Eipers-Smith, K. Waters, and J.A. Schultz, J. Am. Ceram. Soc. 76, 284 (1993). @footnote 2@ V. Bykov, C. Kim, M.M. Sung, K.J. Boyd, S.S. Todorov, and J.W. Rabalais, Nucl. Instr. And Meth. In Phys. Res. B 114, 371 (1996).

11:20am **SS2+AS+PS-WeM10 Depth Information in Direct Recoiling Peak Shapes: Simulations from Model Surfaces***, **M. Tassotto,*** Oregon State University*; P.R. Watson,* Oregon State University, U.S.

Direct recoil spectrometry (DRS) has been used in the past to study adsorbate surface structures, chemisorption processes, and average orientations of molecules at surfaces. In these studies, DRS has experimentally been proven to be very surface sensitive. Information on surface structure and composition is primarily based on the analysis of DR peak intensities from the time-of-flight (TOF) spectra. These DR peaks frequently exhibit long tails to higher TOF which often overlap with neighboring peaks. It is common practice to obtain intensities from TOF spectra by integrating the DR peak areas over narrow time windows. Unfortunately, quantitative analysis is complicated by a lack of accurate background removal and only the use of relative intensity variations is possible. In this study, the MARLOWE computer code has been applied to calculate the trajectories of atoms recoiling from both simple and more complex model surfaces (diamond and alkane polymers, respectively) while the depth from which recoiled particles originated was recorded. The DR peak itself as well as the long TOF tail to lower energies contain depth-related information. Near the peak maximum recoils originate from mainly the first atomic layer, supporting the high surface sensitivity of DRS. The initial portions of the tail of the peak provide an approximate atomic depth profile but at longer TOF the tail contains recoils that were produced by several mechanisms from a wide variety of depths. The trajectory calculations have been converted to actual TOF spectra which allows comparison with experimental data from the literature. Here it is important to account for varying detector efficiencies as well as broadening of the simulated DR peak due to the finite pulse width of the ion beam. The MARLOWE calculations make DR peak deconvolution possible. This leads to accurate background removal in determining atomic ratios.

11:40am **SS2+AS+PS-WeM11 Hyperthermal-energy Ion Scattering on Si(100)***, **C.L. Quinteros**, S.I. Tzanev, D.C. Jacobs,* University of Notre Dame

Ion-surface scattering experiments on a Si(100) surface are presented, introducing a new gas/surface experimental system with unique capabilities. Using a Colutron type source, an ion beam with energies between 5-300 eV can be generated. The ions are extracted, accelerated, mass-selected by a Wein filter, decelerated and focused on the surface target. Scattered ions and neutral products are mass- and energy-resolved with a fully rotatable, differentially-pumped detector that includes an ionization source for detection of neutrals, a cylindrical electrostatic analyzer for energy selection, and a quadrupole mass spectrometer for mass selection of the energy-filtered particles. Incident angles between 0-90° and scattering angles between 0-150° can be accessed by independent rotation of the sample manipulator and the detector. A complement of surface analysis techniques (LEED, Scanning Auger Electron Spectroscopy, X-Ray Photoelectron Spectroscopy, and a Kelvin Probe) monitor surface modifications resulting from ion-beam exposure. The surface sample can be cooled to 80K through a liquid nitrogen reservoir or resistively heated to 1000K. The hyperthermal energy range spans from thermal energies (<1eV), where chemical interactions produce inelastic scattering events, to the low energy regime (1-5 keV), where predominantly elastic scattering occurs. We present scattering results for a series of different projectiles on Si(100) that bridge these two energy regimes. The charge state and energy distributions of the scattered products are reported as a function of collision energy and scattering angle.

Wednesday Afternoon, October 27, 1999

Applied Surface Science Division
Room 6A - Session AS-WeA

Oxides and Insulators

Moderator: C. Pantano, Pennsylvania State University

2:00pm **AS-WeA1 The Pleasure and Pain of Working with Insulators***, **D.R. Baer**, S.A. Chambers, G.C. Dunham, M.H. Engelhard, S.A. Joyce, A.S. Lea, T.M. Orlando,* Pacific Northwest National Laboratory **INVITED**

The detailed understanding of the surface properties of insulating materials is considerably less well developed then that for metals and semiconductors. Some of the reasons for this include the difficulty in getting clean well defined surfaces, the fact that many analysis methods use beams that damage the materials and complications in data collection and analysis due to charge buildup on the samples. The good news is that these materials are very interesting, they are technologically and environmentally important and not as many people are examining them as other materials. Even for analysis of "real" materials and solving applied problems, understanding damage processes, having relevant "reference" spectra, and appropriately dealing with charging effects can mean the difference between success or failure. This presentation will describe some of our research interests involving insulating materials along with a selection of the problems (some with solutions) we have encountered. The presentation will give some examples of deliberate and unintentional beam damage, consequences of heating surfaces, creating and observing defects, methods to prepare "good" and "bad" surfaces, handling charging on difficult materials, and consequences of ion depth profiling. Materials to be discussed will include oxidized forms of Ti, Fe, Pb, Al, and Mg. Examples will include uses of AES, XPS, MBE, and SPM. This work is supported by the Division of Geosciences, Office of Science, U. S. Department of Energy and most of the research performed at the W. R. Wiley Environmental Molecular Sciences Laboratory, a national scientific user facility sponsored by the U.S. Department of Energy's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory.

2:40pm **AS-WeA3 Surface Segregation in NixCo(1-x)O and MnxCo(1-x)O Solid Solutions***, **M.A. Langell**,* University of Nebraska*; M.W. Nydegger,* Pace Analytical Corporation*; F. Gevrey,* Univ. Framche Comte, France*; G. Couderc,* Univ. Lyon, France

Because of the similarity in crystal structure and compatible nature of their cations, many transition metal oxides systems are miscible over a wide range of composition. For these systems, the bulk structure was investigated by powder x-ray diffraction as early as the mid 1940's, and they are generally observed to follow Vegard's law. We have measured the surface composition of two rocksalt monoxide systems, NiO/CoO and MnO/CoO, which form bulk homogeneous solid solutions over the entire range M@subx@Co@sub(1-x)@O (M =Ni or Mn) of 0@<=@x@<=@1. Surface analysis has been performed with Auger and x-ray photoelectron spectroscopy, the latter of which also provides information on the chemical nature of the cations at the surface of the solid solution. Unlike the bulk material, the surface of both systems shows distinct evidence for segregation of one cation at the expense of the other and appears to be related to the formation of a spinel phase. In the case of the NiO/CoO system the spinel composition is NiCo@sub2@O@sub4@, and for the MnO/CoO system the composition agree with the spinel CoMn@sub2@O@sub4@. Information is also obtained on the octahedral and tetrahedral site occupancy of the cations and on their formal oxidation states.

3:00pm **AS-WeA4 Dynamics of CO Adsorption on O-ZnO: a Molecular Beam Study***, Th. Becker, Ch. Boas, **U. Burghaus**, Ch. Woell,* Ruhr-Universität Bochum, Germany

We present measurements of the initial adsorption probability, S@sub 0@, as well as its coverage dependence, S(@THETA@@sub CO@), of CO on oxygen terminated ZnO(0001) surfaces. Two different substrates with significantly different density of defects, as determined by He atom scattering, were investigated. Using a well defined molecular beam of CO seeded in He the He atom reflectivity could be monitored simultaneously with the flux of backscattered CO molecules. These results allow to separately determine the total sticking coefficient averaged over the whole surface (using the King and Wells method) and the sticking coefficient on flat terraces. Measurements were carried out for different impact energies (48 meV < E@sub i@ < 0.74 eV) and surface temperatures (77 K < T@sub s@ < 800 K). The crystallographic structure and chemical composition of the surfaces have been characterized by LEED, He atom scattering, and XPS. The shape of the S(@THETA@@sub CO@,T@sub s@) curves points to a precursor mediated adsorption, since, for medium (100 - 180 K) surface temperatures S(@THETA@@sub CO@) remains approximately constant up to saturation coverage, @THETA@@sub sat@. For low adsorption temperatures (70 - 90 K) a rather unique shape of S(@THETA@@sub CO@) has been observed, namely an increase of S(@THETA@@sub CO@) with @THETA@@sub CO@ followed by an abrupt decrease when approaching @THETA@@sub sat@. S@sub 0@ is essentially independent of T@sub s@ and decreases linearly with E@sub i@, consistent with a precursor-mediated adsorption and a decreasing probability of adsorption into the precursor state, respectively. The results indicate that the presence of defects does affect the CO sticking probability.

3:20pm **AS-WeA5 Compositional Heterogeneity in Cerium-Based Mixed Oxides Observed by XPS***, **G.W. Graham**,* Ford Motor Company, US*; C.L. Roe,* GE Lighting Division*; L.P. Haack, A.M. Straccia,* Ford Motor Company

It is argued that compositional heterogeneity in certain reducible mixed oxides, like Ce@sub1-x@Zr@subx@O@sub2@, can be inferred from a variation in the metals ratio, as measured by XPS, between fully oxidized and partially reduced states of the oxide, provided that the characteristic linear dimension of the heterogeneity is at least as large as the typical electron inelastic mean free path. The argument is supported by experimental results from two examples involving mixed phases, one in which the length scale is 100 nm and the other in which the domains are too small for detection by standard x-ray diffraction.

3:40pm **AS-WeA6 The Formation of Magnesium Oxide Layer using the MgO Precursor Solution and its Secondary Electron Emission***, **J.H. Lee**,* Samsung Advanced Institute of Technology, Korea*; T.W. Jeong,* Myong Ji University, Korea*; S.G. Yu, H.W. Son, S.H. Jin, W. Yi, Y.S. Choi,* Samsung Advanced Institute of Technology, Korea*; D. Jeon,* Myong Ji University, Korea*; J.M. Kim,* Samsung Advanced Institute of Technology, Korea

The thin layer magnesium oxide having a secondary electron emission coefficient (@delta@) value over 5 is obtained by a spin coating of the MgO precursor solution. The solutions are prepared as an aqueous base using magnesium formate and poly vinly alcohol, or as an organic base using magnesium acetate in 1,3-propanediol which is polymerized by magnesium methoxide. Alkali metal ions including Cs ion are doped by dissolving metal formate or acetate salts additionally in the above solutions. The firing condition, 450 C for 2 hours, is determined by the thermogravimetric analysis data of the dried bulk solution. The XRD measurement of the powder from a firing of the bulk solution at this temperature confirms the MgO crystal structure. The MgO films on Si(100) or ITO glass substrates prepared by a spin coating at 4000 rpm for 40 sec followed by firing at 450 C for 2 hours result in the thickness of 300 Å with a good roughness for a @delta@ value over 5. The doping effect of alkali metal ions of the MgO film is discussed on the regards of the secondary electron emission. The surface morphology and composition are characterized by SIMS, AFM, and SEM. This method allows an easy processing approach with a relatively high @delta@ value, as well as a variety of application into many kinds of structural device such as a microchannel plate with high aspect ratio.

4:00pm **AS-WeA7 Reactivity of Formic Acid (HCOOD and DCOOH) at Uranium and UO2 Surfaces***, **M.T. Paffett**, W.L. Manner,* Los Alamos National Laboratory

Interactions of DCOOH and HCOOD with uranium and UO2.0 surfaces have been examined using surface specific techniques of thermal desorption mass spectroscopy (TDMS), x-ray photoelectron spectroscopy (XPS), and static secondary ion mass spectroscopy (SSIMS). Formic acid dissociates on both surfaces below 100 K to yield surface formate in relatively high yield. On the clean uranium surface a wide range of products are observed after annealing to 200 K which include formate, hydroxyl, and C-Hx (C-Dx,), Oads, and Hads(Dads) groups. Adsorbed formate decomposes by 300 K increasing the concentration of the remaining surface products (especially C-Hx (C-Dx) type moieties). The only gaseous species created in high yields from the clean surface upon annealing are H2, HD, and D2. A small amount of water and methane desorb at higher temperatures. Between 100 and 300 K the predominant species on the UO2.0 surface is surface formate and hydroxyl groups. The presence of surface oxygen stabilizes the formate groups to further dissociation in comparison to the clean uranium surface. Hydroxyl groups react between 300 and 350 K to release water from the surface. Adsorbed formate groups decompose between 400 and 500 K to release CO, COH2 (COD2) groups. Carbon was not detected on the surface by XPS after annealing to 500 K indicating that all carbon containing species either desorb in the form of CO-containing products or dissolve into the surface.

4:20pm **AS-WeA8 Characterisation of Ceramics Thin Films Deposited by Plasma Assited CVD***, **G. Ceccone**,* European Commission Joint Research Centre, Italy*; P. Colpo,* European Commission, Joint Research Centre, Italy*; M. Baker, P.N. Gibson, P. Sauvageot, F. Rossi,* European Commission Joint Research Centre, Italy

The use of ceramics in biomedical applications has received large attention during the last two decades. In particular, ceramics and glasses have important applications as orthopedic and dental implants. However, since most of bioactive ceramics and glasses are relatively brittle they have to be applied as a coating on high-strength material such as titanium. In this paper, we report the possibility to depositing zirconia coatings by using Inductively Coupled Plasma Assisted CVD technique. Deposition have been performed in a cylindrical ICP reactor from tetra (tert-butoxy)-zircon precursor diluted in argon and oxygen. A 13.56 MHz generator was used for sustain the plasma, whilst the substrate negative bias voltage was controlled by an independent RF generator. The coating microstructural characteristics were investigated by SEM/EDX; XRD was used to assess the coating crystal structure, whereas the coating composition and stoichiometry was investigated by AES and XPS. The mechanical properties of the films have been assessed by nanoindentation and scratch tests. Zirconia coatings having a thickness between 1 and 10µm, and with a maximum hardness of 13GPa have been deposited under different plasma conditions. Correlation between the deposition parameters, such as the gas composition, RF biases, and RF power, and coating properties have been investigated. AES measurements indicate that films having a stoichiometric composition can be deposited over a large range of gas composition, whilst the crystalline structure and mechanical properties of the film are strongly dependent on the ion bombardment energy. The possibility of tailoring the coating characteristics by controlling the ion energy, i.e. the substrate negative bias is presented and discussed.

4:40pm **AS-WeA9 XPS and UPS Characterization of Single Crystal NaNO@sub 3@ and NaNO@sub 2@: Influence of Laser Irradiation at 248 nm***, **C. Bandis**, S.C. Langford, J.T. Dickinson,* Washington State University

Inorganic nitrates are susceptible to radiation damage, including laser and x-ray irradiation. The critical role of radiation induced chemistry is studied utilizing monochromatised X-ray photoelectron spectroscopy (XPS) and He II (40.8 eV) ultraviolet photoemission spectroscopy (UPS). Photoelectron emission from single crystal NaNO@sub 3@ and NaNO@sub 2@ cleaved and laser or x-ray irradiated surfaces shows that the observed changes in the spectra due to laser irradiation are similar with those observed due to X-ray exposure. Our observations suggest that in both cases (laser and X-ray irradiation) the NaNO@sub 3@ decomposition is initiated by the pi-pi* transition in the NO@sub 3@@super -@ anion. Direct comparison of our experimental UPS and XPS valence band electron energy distributions with recent calculations of the total density of states shows good agreement between theory and experiment for both NaNO@sub 3@ and NaNO@sub 2@. We also report on the influence of such surface modification on the laser desorption of ions and neutrals from cleaved NaNO@sub 3@ single crystal surfaces. This work was supported by the Department of Energy (DE-FG03-98ER14864) and the National Science Foundation (DMR-9503304).

5:00pm **AS-WeA10 Surface Defects on Amorphous Aluminum Oxide Films as Corrosion Initiation Sites***, **K.R. Zavadil**, J.C. Barbour, K.-A. Son,* Sandia National Laboratories

The surface activity of chloride ions is viewed as one parameter responsible for corrosion initiation and subsequent breakdown of native aluminum oxide films on aluminum surfaces. One approach to understanding the role of chloride, as well as other corrosion initiators and inhibitors, is to study the surface of tailored oxides that mimic the properties of naturally occurring passive oxides on aluminum. We generate amorphous oxides ranging from tens to hundreds of angstroms thick by exposing electron beam deposited Al films to an O@sub2@ electron cyclotron resonance (ECR) plasma. Surfaces defects in the form of oxygen vacancies are generated at low energy doses of both electron (electron stimulated desorption) and ions (preferential O sputtering). A comparison is made between the activity of vapor phase and solution phase H@sub2@O and Cl at the defective oxide surface by conducting vacuum and solution experiments with a contiguous electrochemical cell. Irradiation and hydration effects are tracked using a combination of Auger electron and x-ray photoelectron spectroscopies as well as temperature programmed desorption. We show that vacancies are active toward vapor phase Cl sorption resulting in surface Cl concentrations of 10@super13@ to 10@super14@ atoms×cm@super-2@. Cl is desorbed from these vacancies at temperatures below 570 K and is displaced by H@sub2@O vapor at room temperature. Defective surfaces show a greater susceptibility to corrosion as measured by a lowering in the pitting potential in 50 mM NaCl solutions. The role of the vacancies in solution appears to be an increase in surface charge resulting in enhanced Cl@super-@ sorption. We find measurable increases in surface oxygen for defective, hydrated alumina surfaces consistent with a surface charge increase. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the U.S. Department of Energy under contract DE-AC04-94AL85000.

Applied Surface Science Division
Room 6A - Session AS-ThM

Real World Surface Analysis

Moderator: T. Barr, University of Wisconsin, Millwaukie

9:00am **AS-ThM3 The Real World: Surface Analysis Applications and Innovations in Industry*, S.J. Pachuta,*** 3M **INVITED**

The term "real world" surface analysis is often used in opposition to "academic" surface analysis. The distinction is conventionally viewed as being a matter of single crystal studies under ultra high vacuum in the academic case, vs. everything else in the real world case. In reality there is, of course, some overlap between the two, but it is true that industrial analysts must often deal with unknown materials under less than ideal conditions. The following is a far from exhaustive list of the challenges: samples with fingerprints and surface environmental contamination; volatile materials; buried layers, both elemental and organic; complex mixtures such as copolymers and blends with multiple additives; submicron features and defects, possibly on the surface but often buried; insulators; samples too large for most vacuum systems, but which must be preserved and cannot be cut; inhomogeneous materials. More often than not, a multi-instrument approach is needed to address industrial surface analysis problems. The three techniques of x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) comprise the backbone of most industrial surface analysis laboratories. Other techniques like infrared spectroscopy and atomic force microscopy are also being increasingly utilized. An important--and sometimes overlooked--aspect of surface analysis is sample preparation, which often turns out to be the key to solving a problem. This talk will use examples from a diverse industrial laboratory to illustrate the synergism between the various surface analysis methods. Emphasis will be placed on organic materials, since a large part of industrial analysis is concerned with polymers and other organics. New sample preparation methods for XPS and time-of-flight SIMS will be described which extend the capabilities of these techniques.

9:40am **AS-ThM5 Effect of Sputtering Gas on Cleaning Al-Based Intermetallics and the Determination of Surface Compositions based on Auger Analysis*, C.J. Jenks,*** *T.E. Bloomer, M.J. Kramer,* Ames Laboratory*; J.W. Burnett,* Iowa State University*; D.W. Delaney, T.A. Lograsso, M.F. Besser, D.J. Sordelet, P.A. Thiel,* Ames Laboratory

Argon is the typical gas of choice for sputtering single crystals in preparation for ultrahigh vacuum studies. However, the use of argon when cleaning Al-based intermetallics leads to preferential etching of Al. This can be a problem because of potential phase changes and the need for a consistent surface composition after annealing. We have examined the extent of this preferential etching as a function of ions/cm@super 2@ for helium, neon, argon, and krypton. The intermetallic substrate has a bulk composition of Al@sub 72.8@Pd@sub 18.6@Mn@sub 8.6@. We find for this material that the steady state Al concentration at the surface is about the same for all the sputtering gases examined. However, the number of ions/cm@super 2@ (which is related to time) depends on the sputtering gas used. Also discussed will be the determination of surface composition of Al-based intermetallics by Auger Electron Spectroscopy. For these materials, in particular, the sensitivity factors will differ greatly between the pure elements and the compound matrix because of changes in electron escape depth, electron backscattering, and atomic density. We find that the use of certain standards can lead to erroneous results.

10:00am **AS-ThM6 Failure Mechanisms of Adhesively Bonded Hot Dipped Galvanised Steel Studied by Small Area XPS*, R.G. White,*** VG Scientific, UK*; M.F. Fitzpatrick, J.F. Watts,* University of Surrey, UK

One of the most important requirements of an adhesive joint is the retention of strength for an acceptable time on exposure to a hostile environment. Durability is recognized as one of the most significant problems in the adhesive bonding in industry. In a previous paper, small area XPS established that electrochemistry was responsible for initial bond degradation in a phosphated hot dipped galvanised steel (HDGS) lap joint.@footnote 1@ This paper reports a surface analysis investigation of the failure mechanism of adhesively bonded hot dipped galvanized steel that has been exposed to a hostile environment. The failed lap shear joints show areas of apparent interfacial failure, however, these regions are limited to thin strips at the end of the overlap. These "initiation zones" seem to be a result of environmental exposure and appear to act as initiation sites for crack propagation on mechanical testing, acting as "notch like" features. The study of these areas of the failed surface using small area XPS (15 micron resolution) is reported in this paper, with a view to establishing the role of electrochemical activity at the crevice tip and its role in the subsequent joint failure. Acknowledgement : The authors wish to thank British Steel Strip Products and Welsh Technology Centre for the provision of a Research studentship (MFF) and for permission to publish this paper. @FootnoteText@ @footnote 1@J.F.Watts and M.F.Fitzpatrick Surf. Interf. Anal. in press.

10:20am **AS-ThM7 Novel X-ray Sensor Suite for In Situ Optimization of Thin Film Architectures*, L.L. Fehrenbacher,*** *D. Palaith, C. Deaton, J. Ullrich,* Technology Assessment & Transfer, Inc.

Advances in compact, high energy x-ray sources and sensitive detectors are creating new opportunities for the use of x-rays for real time and near real time interrogation of thin film properties. A design approach that combines x-ray diffraction, florescence and reflectivity measurements with a thin film deposition system is described. Phase, composition, surface and interfacial roughness, thickness and density of thin films can now be monitored during a thin film deposition process enabling improved control over process deposition parameters. Details of the equipment and examples of the systems used for rapid development of new multilayer thin film architectures as well as production control are provided.

10:40am **AS-ThM8 A 300mm SAM, with EDX and FIB for Full Wafer Defect and Thin Film Characterization*, Y. Uritsky,*** Applied Materials, Inc.*; C.R. Brundle,* Applied materials, Inc.

As design rules shrink and thin film stacks get thinner, the semiconductor equipment manufacturing industry is forced to move to more sophisticated approaches for its particle defect and thin film characterization needs, including surface and thin film analysis. In the past we have occasionally supplemented our full wafer (200 mm) SEM/EDX small particle analysis work by SAM, using small cut up pieces of the wafer. We have now installed the first full 300 mm wafer SAM (Smart 300 from PHI), on which we also have traditional EDX and also FIB. The capabilities of this instrument are briefly described here and examples are given of its use to a) find small defects based on navigation from light scattering files, b) comparatively analyze small particles using Auger, EDX, and FIB sectioning, and c) profile films to examine interfaces. With respect to a) above, since light scattering files are usually quite inaccurate (the predicted coordinates can easily be in error by 100's of µm's), it can be very time-consuming, if not impossible, to re-find very small particles (0.1 µm) with low SEM or Auger contrast. Use of a 300 mm capable dark field optical bench/wafer marker (MicroMark 5000) system to update the particle coordinates with +/- 5 µm) accuracy and/or to create laser-made fiducial marks, can accelerate the subsequent particle re-detection/analysis SAM procedure by a factor of 10. Another particular concern to us, since it is a widely used element in semiconductor processing and is very aggressive, is the relative ability of Auger, EDX, and FIB sectioning Auger and EDX, to reliably detect F as opposed to removing it under the probe beam. This is discussed.

11:00am **AS-ThM9 A Study of the Surface Chemistry and Physical Properties Related to Adhesion of the Polyimide Passivation Layer by XPS, FTIR, and Contact Angle Measurements*, T. Jiang*,** Micron Technology Inc.*; C.A, Bradbury,* Micron Technology Inc., US*; M. Canavan,* Micron Technology Inc

Adequate die-to-leadframe adhesion is necessary for lead on chip (LOC) package integrity during and after the manufacturing process. Poor adhesion may result in a variety of defects such as die adhesion failure, marginal wire bond, broken wire, and bent leads ultimately leading to electrical failure. Adhesion between the LOC tape and the polyimide passivation is affected by the surface properties of both materials. Understanding the relationships between these properties is important for the elimination of adhesion failures at die attach and for the continuous improvement of the manufacturing process. To this end, die which fail at attach are analyzed and compared with die which exhibit good adhesion characteristics. This study focuses on the surface chemistry and physical properties of the passivation layer using X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), atomic force microscopy (AFM), and surface energy. Molecular concentrations and orientations are investigated and related to adhesion failures at die attach.

11:20am **AS-ThM10 Diffusion of Large Molecules on Metallic Surfaces using TOFSIMS*, R. Avci*,** *S.E. Maccagnano,* Montana State University*; G.L. Gresham, G.S. Groenewold,* Idaho National Engineering and Environmental Laboratory

The environmental contamination of clean surfaces creates challenging problems in practical surface analysis. In most cases the contamination is caused by a contact between a dirty and a clean surface and the subsequent diffusion of the contaminant over the clean surface. In this presentation a semi-quantitative study of the diffusion process of large molecules such as polydimethylsiloxane and tributyl phosphate on metallic surfaces will be presented. Using imaging time-of-flight secondary ion mass spectroscopy (ToFSIMS) we have monitored the diffusion of these molecules by first absorbing them on the surface of a fiber such as linen and nylon and then placing the fiber in contact with a metallic surface such as a gold-coated silicon wafer. ToFSIMS spectra are taken as (a) a function of distance from the contact point and (b) a function of time from moment of contact to determine the diffusion properties of these molecules on the surface. Our preliminary observations show that these molecules rapidly diffuse away from the contact point on the surface of the metal.

11:40am **AS-ThM11 Identification of Surface Chemical Functional Groups in Reverse Osmosis Membranes: An X-ray Photoelectron Spectroscopy Study***, **S.D. Beverly**, S. Seal, S.K. Hong,* University of Central Florida

Membrane filtration including reverse osmosis (RO) has emerged as a viable drinking water treatment technology that offers a versatile approach to meeting multiple water quality objectives. Due to fouling and membrane failure, however, wide use of membrane processes for municipal water supplies has not become the reality that it could be. This study is an attempt to identify surface functional groups and chemical changes in surfaces of RO membranes during operation, which would give clues to the nature of the membrane failure. Since the depth of the RO membrane skin layer is less than 50 angstroms, X-ray Photoelectron Spectroscopy (XPS) was chosen to be a practicable analytical tool for this research study. Three commercial RO membranes made of organic polymers of polyamide or cellulose acetate were investigated. These membranes were chosen because of specific characteristics such as chlorine degradation, biological degradation, or fouling resistant coatings. For each membrane, a baseline spectrum was taken and then a sample of the membrane used to treat river water in Tampa, Florida was tested. Each sample was thoroughly rinsed in DI water and allowed to dry before XPS analysis. XPS analysis clearly showed a distinct uptake of chlorine in the polyamide membrane, a probable reason for failure in the drinking water industry. The cellulose acetate membrane showed evidence of amino acids, an indicator of digestion by an unidentified microbe. Based on the findings of this report, future studies are being considered to further investigate chlorine uptake by RO membranes. The studies will include charting chlorine uptake over time and finding limiting factors to chlorine uptake.

Surface Science Division
Room 606 - Session SS1+AS+BI-ThM
Self-Assembled Monolayers

Moderator: N.D. Shinn, Sandia National Laboratories

8:20am **SS1+AS+BI-ThM1 Two-Dimensional Phase Transitions in Amphiphile Monolayers***, **G.E. Poirier**,* National Institute of Standards and Technology

Recently scientists have explored methods of constructing complex chemically patterned surfaces with the goal of making novel biosensors or of realizing lab-on-a-chip technology. In order to design patterned monolayers it is important to understand how these molecules behave in two dimensions, what is the molecular packing of the surface phases and which phases coexist in thermodynamic equilibrium. The goal of this presentation is to describe the two-dimensional structural phases of decanethiol monolayers. Our studies were conducted using gas-phase transport of decanethiol onto clean Au(111) in an ultrahigh vacuum scanning tunneling microscope. With increasing surface coverage, the monolayer sequentially adopts six discrete structural phases. At low surface coverage, decanethiol exists as a lattice gas. With increasing coverage the molecules sequentially condense into islands of three discrete commensurate crystalline lattices, each characterized by alignment of the molecular axes with the surface plane, but with discretely increasing degrees of out-of-plane interdigitation. Above saturation coverage of the densest surface-aligned phase, the monolayer undergoes an edge-mediated melting transition. The c(3x2/3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleates and grows from this liquid. These studies provided a detailed, real-space picture of the coverage-dependent phases and phase transitions of alkanethiol molecular monolayers on Au(111).

8:40am **SS1+AS+BI-ThM2 Surface Phase Transitions of Asymmetric Dialkyl Disulfide Self-Assembled Monolayers***, **M. Hara**, K. Kamei, T. Araki, K. Fujita, W. Knoll,* Frontier Research Program, RIKEN, Japan

Adsorption and desorption processes of asymmetric dialkyl disulfide (hexyl octadecyl disulfide: C6-SS-C18) self-assembled monolayers (SAMs) on Au(111) have been investigated by surface plasmon resonance (SPR), mass spectroscopy (MS), thermal desorption spectroscopy (TDS), and scanning tunneling microscopy (STM). Formation of C6-SS-C6 and C18-SS-C18 dimer species in the monolayer and also in the solution through dimerization and exchange processes has been confirmed during the monolayer growth. In the TDS spectra for shorter immersion SAMs, C6 monomer species showed the strong peaks, and gradually C6-SS-C6 dimer and C18 monomer peaks become stronger for longer immersion. Phase-separated domains of pure C6 and pure C18 striped phases have been visualized in the initial growth stage by STM and the area of the C6 domain was larger than that of C18 one. These results suggest that S-S bonds were cleaved when disulfides adsorbed on Au surface followed by the surface diffusion to form phase separation before standing-up SAM formation. After the C6-rich SAM growth, molecules are dimerized and then exchange process starts from the weakly bound C6-SS-C6 dimers toward C18-rich SAM. SPR kinetics studies also showed the double exponential growth which is different from usual Langmuir adsorption isotherm. Following those results, we propose more detailed surface phase transition model of alkanethiol SAM growth through the dimerization and the exchange processes.

9:00am **SS1+AS+BI-ThM3 Structure, Bonding and Reactivity of Self-assembled Monolayers***, **G.J. Leggett**, B.D. Beake, N.D. Brewer,* UMIST, UK*; E. Cooper,* Glaxo-Wellcome, UK*; D.A. Hutt,* University of Loughborough, UK

Two approaches to the characterisation of the nature of the sulfur bonding environment in self-assembled monolayers (SAMs) have been explored: sulfur K-edge surface extended X-ray absorption fine structure (SEXAFS) and static secondary ion mass spectrometry (SIMS). S K-edge SEXAFS has proved highly effective for SAMs on Ag and has confirmed that the sulfur adsorbs with threefold coordination during both solution-phase adsorption onto polycrystalline Ag and gas-phase adsorption onto Ag(111) single crystal surfaces. There is no change in the S adsorption site with coverage. Static SIMS has yielded powerful insights into the effect of electron beam bombardment on SAM structure. A complete loss of all gold-molecular fragments from the spectrum is observed after small doses of electrons, indicating a rapid alteration of the sulfur bonding environment, due either to S-C bond scission or, more likely, to oxidation of thiolates to disulfides. Changes in Au-S bonding during the formation of the low coverage phase of butanethiol on Au have also been studied by static SIMS. Photo- and air-oxidation rates are influenced by the adsorbate alkyl chain length; rates of both processes decrease with increasing chain length due to increasing SAM ordering. The nature of the terminal group also affects rates of oxidation, and has a profound influence on the stability of the SAM. Hydrogen bonding between neighbouring terminal groups leads to significant stabilisation. Friction coefficients may be measured for SAMs using friction force microscopy. These decrease with increasing alkyl chain length, and are higher for adsorbates with polar terminal groups. Oxidation of methyl terminated SAMs leads to an increase in the coefficient of friction, interpreted in terms of the collapse of film order following head group oxidation. The rate of increase in the coefficient of friction is faster for short chain SAMs than long-chain SAMs, in agreement with the findings of static SIMS studies.

9:20am **SS1+AS+BI-ThM4 Structure of Partially Fluorinated n-alkanethiols on Polycrystalline Gold and Silver Surfaces***, **S. Frey**,* Universität Heidelberg, Germany*; K. Tamada,* National Institute of Materials and Chemical Research, Japan*; K. Heister, M. Zharnikov, M. Grunze,* Universität Heidelberg, Germany

The physical and chemical properties of self-assembled monolayers (SAM) of alkanethiols (AT) are noticeably affected by partial fluorination of the hydrocarbon chain. We have studied the structure of SAMs formed from partially fluorinated alkanethiols (PFAT) CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub n@SH with different hydrocarbon chain length (n = 2, 11 and 17) on Au and Ag coated silicon wafers. The objectives of our experiments were (i) to find out whether PFAT form ordered and densely packed SAMs on these substrates, (ii) to determine the individual conformation and orientation of the hydro- and fluorocarbon parts in the molecules, and (iii) to clarify the influence of the headgroup-metal bond (RS-Au or RS-Ag) on the film structure. The PFAT films were characterized by atomic force microscopy, infrared reflection absorption spectroscopy, X-ray photoelectron spectroscopy, and angle resolved near edge X-ray absorption fine structure spectroscopy. PFATs were found to form highly ordered and densely packed SAMs on polycrystalline Au and Ag. The hydrocarbon and fluorocarbon chains of the adsorbed PFATs retain the expected planar zigzag and helical conformation of the bulk materials, respectively. The fluorocarbon chains, which are oriented almost perpendicular to the substrates for CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub 2@SH, assume a more tilted orientation in PFAT SAMs with longer hydrocarbon moieties. As found for the AT on Ag and Au, the hydrocarbon part in the PFAT films exhibits smaller tilt and twist angles on Ag as compared to the Au substrates. Considering the reduced van der Waals interaction between the hydrocarbon chains in PFAT as compared to neat AT SAMs (due to the sterical constraints provided by the fluorocarbon chains), the differences in tilt and twist angle appears to be associated with the different character of the headgroup-substrate bonding on Au and Ag. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie through grant No. 05 SF8VHA 1.

9:40am **SS1+AS+BI-ThM5 Controlling the Placement of Molecules in the Self Assembly and Directed Assembly of Organic Monolayers***, **P.S. Weiss**, D.L. Allara, L.A. Bumm, J.J. Jackiw,* The Pennsylvania State University **INVITED**

We manipulate and measure the structures of monolayer films in order to tune their properties. This is accomplished by controlling the defect type and density in the films. We then process the films to insert single molecules, to insert bundles of molecules, or to graft new molecular terraces onto existing domains by using these defects to advantage. The inserted molecules can serve as the anchor points for polymerization; this allows us to choose to produce single polymer dots or isolated polymer brushes. We connect our scanning tunneling microscopy measurements to electron transfer phenomena which are ubiquitous in such areas as biochemistry and electrochemistry by separating the transconductance into components arising from transport through the molecule vs. the tunneling gap outside the film. We show how these components can be measured independently. We prepare films predicted to have many equivalent defect sites so as to provide identical matrix isolation environments for single molecular wire candidates. We also prepare films with well defined interfaces between separated components so that insertion, deposition, or reaction can be directed to these molecularly sharp boundaries.

10:20am **SS1+AS+BI-ThM7 Protein Adsorption to Model Surfaces: Probe Adhesion Between Fibrinogen and Patterned SAMs***, **L.F. Pardo**, T.B. Boland,* Clemson University

Interactions between blood and an artificial surface induce a rapid, thrombogenic response believed to be mediated by protein adsorption. In this study, atomic force microscopy (AFM) was used to measure directly non-specific forces between proteins and functionalized surfaces. A protein-modified AFM cantilever tip was used to probe of interactions between a model substrate and a single protein. Model surfaces consisted of both simple and microcontact-printed, -OH, -COOH, and -CH3 terminated self-assembled monolayers (SAMs) of alkanethiols on gold. Fibrinogen was used as the model protein due to its significance in biomaterial-mediated inflammatory responses. It was tethered to the probe tip using a synthetic polypeptide (polyserine). Various approaches were taken to link polyserine to a self-assembled monolayer on a gold substrate. Ellipsometric and vibrational spectroscopic measurements indicated that successive carbodiimide activation of a carboxyl-terminated alkanethiol and polyserine allowed for the successful formation of a polyserine-tethered fibrinogen film. The SAMs, polyserine and fibrinogen films were characterized by ellipsometry and contact angle measurements. Both AFM images and measurements will be presented and discussed. An understanding of how fibrinogen interacts under model conditions will give insight into more complicated real systems.

10:40am **SS1+AS+BI-ThM8 Modification of Self-Assembled Monolayers by X-ray, Electron and Thermal Treatments***, **H. Fairbrother**, A. Wagner, K. Han,* Johns Hopkins University

Polymer surface modification strategies are widely used to modify interfacial characteristics, including permeability, wettability, adhesion, friction, wear and biocompatibilty. To better understand the detailed nature of these processes thiol-based self-assembled monolayers (SAMs) adsorbed on Au substrates have been used as models for the polymeric interface. In the case of X-ray modification results from X-ray Photoelectron Spectroscopy on fluorinated SAMs show that the degree of cross-linking can be directly correlated with the appearance of CF groups in the organic film. Additional information from Reflection Absorption Spectroscopy and Atomic Force Microscopy on the impact of X-ray, electron, and thermal modification treatments will also be presented, enabling a detailed picture of the chemical and physical modifications that occur during surface treatments to be constructed.

11:00am **SS1+AS+BI-ThM9 Electron-induced Damage in Thio-functionalized Alkanethiol Monolayers***, **K. Heister**, W. Geyer, S. Frey,* Universität Heidelberg, Germany*; A. Ulman,* Polytechnic University*; A. Gölzhäuser, M. Zharnikov,* Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) of alkanethiols (AT) as lithographic resist require an increased sensitivity of these systems toward ions, X-ray photon or electron irradiation. This effect can be achieved by incorporation of specific molecular groups associated with comparatively weak bonds, such as C-S bond provided by sulfide -S- and sulfone SO@sub 2@- moieties, in the aliphatic chains. We have investigated the damage induced by low-energy electrons in SAMs formed from C@sub 6@H@sub 13@SC@sub 11@H@sub 22@SH (I), C@sub 6@H@sub 13@SO@sub 2@C@sub 11@H@sub 22@SH (II), C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 12@SH (III), and C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 4@OC@sub 5@H@sub 10@SH (IV) on polycrystalline Au substrates using angle-resolved near edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy. Similar to AT SAMs, an irradiation-induced disordering and a dehydrogenation of the pristine films I - IV as well as the desorption of molecule fragments and the transformation of thiolate moieties in a new irradiation-induced sulfur species were observed. The extent of the irradiation-induced events is, however, affected by the introduction of the sulfide and sulfone moieties. An increased extent of the irradiation-induced desorption processes as compared to AT SAMs was found in I and II, which implies that bond scission events predominately occur in the outermost part of AT SAM. Controversially, an additional dipolar interchain interaction provided by the sulfonic entities has a stabilizing influence on the lower part of SAMs II-IV leading to the conservation of the pristine thiolate species responsible for anchoring of the alkyl chains to the substrate. Considering these controversial effects provided by the sulfonic groups the incorporation of sulfide moiety seems to be a better choice to improve the sensitivity of AT SAMs toward electron irradiation.

11:20am **SS1+AS+BI-ThM10 Sensitivity of Alkanethiol Self-assembled Monolayers toward Low-energy Electron Irradiation***, **M. Zharnikov**, S. Frey, K. Heister, M. Grunze,* Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) as lithographic resist involve their exposure to ions, X-ray photons or electrons. We have investigated the damage induced by low-energy electrons in SAMs of dodecanethiolate (DDT), octadecanethiolate (ODT) and perdeuterated eicosanethiolate (PDET) on gold and of ODT on silver using x-ray photoelectron spectroscopy and angle resolved near edge x-ray absorption fine structure spectroscopy. ODT/Au was taken as a reference system, whereas the other SAMs differed from ODT/Au in the length (DDT/Au) and the isotopic composition (PDET/Au) of the alkyl chains and the strength and character of the thiolate-metal bond (ODT/Ag). All systems studied were found to exhibit a qualitatively similar behavior with respect to low-energy electron irradiation. Both the alkyl chains and the S-Au interface are affected simultaneously through the electron-induced dissociation of C-H, C-C, C-S, and metal-thiolate bonds. The most noticeable processes are the loss of the orientational and conformational order, partial dehydrogenation with C=C double bond formation, desorption of film fragments, decrease of thiolate species, and the appearance of new sulfur species. The cross sections for the individual irradiation-induced processes have been determined. The reactions of the alkyl matrix and the S-metal interface to electron irradiation are essentially independent. The extent and rate of thiolate species reduction and new sulfur species formation are mainly determined by the strength and character of the thiolate-metal bond (Au vs. Ag). At the same time, an extent of irradiation-induced desorption of sulfur-containing fragments depends on the alkyl chain length. Only a slight isotopic variation in the irradiation-induced dehydrogenated process was observed.

Surface Science Division
Room 604 - Session SS3+AS+NS-ThM

Novel Surface Probes & Technique Enhancement

Moderator: B.E. Koel, University of Southern California

8:20am **SS3+AS+NS-ThM1 Determination of Sticking Probability and Transition State Energy by Line-of-Sight Detection: Halocarbons on Cu(111)***, **A.S.Y. Chan**, C.A. Clifford, R.G. Jones,* University of Nottingham, UK

We have used a new technique, Line-of-Sight Sticking Probability (LOSSP) to study the reactions of chloroform and 1-bromo-2-chloroethane (BCE) on Cu(111). The sticking probability measurements were made by applying a thermally randomised pressure of the halocarbon above the surface and detecting the reflected flux as a narrow beam of molecules flying in line-of-sight from the centre of the sample surface to the mass spectrometer.@footnote 1@ The general reaction undergone by both halocarbons on the copper surface is: M(gas) -> M(phys) [1] M(phys) -> M(gas) [2] M(phys) -> chemisorbed halogens + gas phase product [3]. By measuring the sticking probability as a function of temperature, we are able to obtain the energies of the transition state M(phys) towards decomposition, which for the non-activated adsorption system of BCE on Cu(111) is ~13 kJ/mol below zero, and for the activated adsorption of chloroform on Cu(111) is ~4 kJ/mol above zero. (Zero energy is defined as the energy of the molecule at an infinite distance from the surface. @FootnoteText@ @footnote 1@ R G Jones and C J Fisher; Surface Science 424 (1999)127.

8:40am **SS3+AS+NS-ThM2 Demonstration of Angle Resolved Auger-photoelectron Coincidence Spectroscopy from a Solid: First Results from the Cu(111) Surface***, **D.A. Arena**, R.A. Bartynski,* Rutgers University*; D. Cvetko, L. Floreano, A. Morgante, F. Tommasini,* Laboratorio Nazionale TASC-INFM, Italy*; A. Attili, A. Ruocco, G. Stefani,* Universita' di Roma, Italy*; L. Marassi, P. Luches,* Universita' di Modena, Italy*; S. Iacobucci,* CNR-IMAI, Montelibretti, Italy

We report the first successful angle-resolved Auger-photoelectron coincidence spectroscopy (AR-APECS) measurements from a solid. These measurements were made at the ALOISA beamline at the ELETTRA synchrotron radiation center in Trieste, Italy. This novel analysis chamber is equipped with seven hemispherical electron energy analyzers mounted on two independent rotatable frames; the arrangement allows for the efficient exploration of different kinematical conditions for the emitted pair of electrons. We measured the angular distribution of Cu L@sub3@VV Auger electrons from the Cu(111) surface in coincidence with Cu 2p@sub 3/2@ photoelectrons emitted at selected angles; these angles correspond to maxima and minima in the photoelectron diffraction (PED) pattern. When the 2p@sub 3/2@ core level is at a PED maximum, the Auger pattern is indistinguishable (within statistics) from the noncoincidence distribution. In contrast, if the 2p@sub 3/2@ photoelectrons are at a PED minimum, the coincidence Auger angular distribution shows additional structure as compared to the noncoincidence pattern. This observation may arise because the two coincidence conditions access different intermediate states. The effects of the lattice may be more pronounced in the Auger angular pattern collected in coincidence with photoelectrons on the PED maximum while the Auger angular distribution acquired in coincidence with the photoelectrons on the PED minimum may exhibit more "atomic-like" behavior. Alternatively, the difference may be a consequence of different probing depths on and off the PED maximum, and hence the sampling of different scattering sites. Experiments to discriminate between these possibilities are currently underway. This work is supported by NSF-DMR 98-01681 and NATO-CRG 97-0175.

9:00am **SS3+AS+NS-ThM3 Multiple Atom Resonant Photoemission: A New Tool for Determining Near-Neighbor Atomic Identities and Bonding***, **A.W. Kay**,* UC Davis and LBNL*; E. Arenholz,* LBNL and UC Berkeley*; B.S. Mun,* UC Davis and LBNL*; J. Garcia de Abajo,* LBNL*; C.S. Fadley,* UC Davis and LBNL*; R. Denecke, Z. Hussain, M.A. Van Hove,* LBNL

A newly discovered resonance photoemission process between neighboring atoms in multielement samples will be presented. Experimental evidence for the effect and possible applications will be considered. In several metal oxides, including MnO, Fe2O3, and La0.7Sr0.3MnO3, we have observed an enhancement in the core-level photoelectron peak intensity associated with one element in the sample (e.g. O 1s) while the excitation energy is tuned through an energetically deeper absorption edge of a second element (e.g. Mn 2p or Fe 2p or La 3d). At the edges of this second element, a 40-100% enhancement in the peak intensity (as an area above inelastic background) of the first element is observed. Furthermore, this peak intensity enhancement exhibits a dependence upon photon energy that closely, but not identically, follows the x-ray absorption coefficient of the second atom. This is evidence of an interatomic or multi-atom resonance photoemission (MARPE) process, that is related to but distinctly different from the much-studied intraatomic or single-atom resonance photoemission (SARPE). Theoretical calculations based on extensions of previous intratomic resonance models have yielded encouraging agreement with our experimental results. The MARPE effect is expected to provide a direct method for determining the atomic identities (atomic numbers) of near-neighbor atoms to the excited atom, as well as providing a new technique for studying bonding and magnetism in molecules, at surfaces,buried interfaces, and perhaps bulk materials provided that secondary fluorescence detection of the resonance can be utilized.@footnote 1@ @FootnoteText@ @footnote 1@ This work was supported by the U.S. Department of Energy, Office of Energy Research, Basic Energy Sciences Division, Materials Science Division, and the Miller Institute (Berkeley).

9:20am **SS3+AS+NS-ThM4 Incident Beam Diffraction in Electron Stimulated Desorption***, **M.T. Sieger**, G.K. Schenter, T.M. Orlando,* Pacific Northwest National Laboratory

The use of electron beams to remove surface-bound atoms and molecules (electron-stimulated desorption, or ESD) is a topic of interest for many disciplines, from semiconductor device processing to astrophysics. We have been studying the role of scattering and diffraction of the incident electron in the initial state of the desorption process. We report calculations and experiments demonstrating that total ESD yields show fine-structure with incident electron direction, consistent with quantum-mechanical scattering and interference of the electron in the initial state of the desorption process. In a time-independent picture interference of the incident plane wave with waves scattered from the crystalline lattice forms an electron standing wave (ESW), having spatially localized maxima and minima in the incident electron density. Whether a particular point on a surface experiences a maximum or minimum depends on the wavelength of the electron, the direction of incidence relative to the crystal axes, and the locations of nearest neighbor atoms. Since the probability of excitation is proportional to the incident electron density at or near the site of the "absorber" atom (the site of the inelastic scattering event), the total ESD rate should depend upon the local atomic structure and the k-vector of the incident wave. The total desorption yield, when measured as a function of incident direction at constant energy, shows oscillations with the symmetry of the absorber bonding site. Since every inequivalent atomic bonding site has a unique pattern of oscillation electron standing wave stimulated desorption (ESWSD) measurements can in principle uniquely determine the bonding geometry of the absorber. We present experimental measurements for chlorinated Si surfaces.

9:40am **SS3+AS+NS-ThM5 Direct Atomistic Observation of Structural Dynamics in Surfaces and Interfaces by Time-Resolved High-Resolution Transmission Electron Microscopy***, **T. Kizuka**,* Nagoya University and Japan Science and Technology Corporation, Japan **INVITED**

Atomic processes of mechanical interaction and gas-phase epitaxial growth were directly observed in situ by time-resolved high-resolution transmission electron microscopy at spatial resolution of 0.1 nm and time resolution of 1/60 s. Nanometer-sized tips of gold and silicon approached, and were contacted, bonded, deformed and fractured inside a 200 kV electron microscope using a piezo-driving. Contact boundaries of a few atomic columns width in gold, silicon/silicon-oxide/silicon tunnel junctions, and quantum dots of silicon/gold-cluster/silicon were produced.@footnote 1@ A few layers near the surfaces and contact-boundaries were responsible for the bonding and separation processes. Atomic scale contact or non-contact type surface-scanning similar to that in scanning probe microscopy was performed by the same method.@footnote 2@ The mechanical removal of one atomic layer was also demonstrated.@footnote 3@ New kinds of atomic scale mechanical tests, such as friction test, compressing, tensile and shear deformation tests were proposed. Gold was vacuum-deposited on (001) surfaces of magnesium oxide inside the electron microscope. Atomic process of epitaxial growth was in-situ observed cross-sectionally. Various types of growth phenomena, such as 'embryo' formation, structural fluctuation, repeated process of truncation and construction of a corner in one gold cluster, secondary nucleation and coalescence, were analyzed in real-space.@footnote 4@ @FootnoteText@ @footnote 1@T. Kizuka, Phys. Rev. Lett., 81 (1998) 4448. @footnote 2@T. Kizuka et al., Phys. Rev., B55 (1997) R7398. @footnote 3@T. Kizuka, Phys. Rev. B57 (1998) 11158. @footnote 4@T. Kizuka et al., Phys. Rev. B56 (1997) R10079.

10:20am **SS3+AS+NS-ThM7 Ionization Mechanisms of Water in High Interfacial Electric Fields***, **D.L. Scovell**[1],* University of Washington, U.S.A*; V.K. Medvedev, C.J. Rothfuss, E.M. Stuve,* University of Washington

High surface fields (Ã1 V/Å) drive many important processes, such as electrochemistry and field emission. The behavior of water in these fields is important because water is the primary component in electrochemical processes and a major contaminant in the vacuum surrounding field emitter arrays in flat panel displays. It is usually assumed that water amplifies the field at the electrode surfaces, but little is known about how water affects the electric field distribution. Field emitter tips lend themselves to the study of the dielectric properties of water because they produce fields as high as 5 V/Å. To better understand the effect of high electric fields on water, numerical analyses have been conducted to model the electric field distribution around a water-covered emitter tip. The calculations include the field-dependence of the relative permittivity of the water adlayer. The model predicts that the dominant field occurs at the vacuum interface in thin water layers and at the metal surface in thick layers. In very thick layers the field at the tip surface is predicted to be greater than the applied electric field. This response is analogous to that assumed for a traditional electrode/electrolyte interface. Experiments have been conducted to verify the predicted trends for thin water layers. In these experiments water was adsorbed onto a platinum field emitter tip under field-free conditions in ultrahigh vacuum. Ionization was examined by isothermal ramped field desorption (RFD) performed as a function of temperature and water layer thickness. The experimental results are consistent with the predicted trends. This work was supported by the Office of Naval Research.

10:40am **SS3+AS+NS-ThM8 Free Electron Laser Nanospectroscopy Interface Applications***, **G. Margaritondo**,* Ecole Polytecnique Fédérale, Switzerland*; A. Cricenti,* Consiglio Nazionale delle Ricerche, Italy*; N.H. Tolk,* Vanderbilt University*; R. Generosi, P. Perfetti,* Consiglio Nazionale delle Ricerche, Italy*; I.D. Aggarwal,* U.S. Naval Research Laboratory

We present the first result of a major effort to investigate the lateral fluctuations of properties of solid interfaces on a microscopic scale. The key elements were the use of a small-tip optics fiber and its coupling with a scanning module; in this way, we achieved and verified the condition of near-field microscopy -- including a lateral resolution much below the wavelength value. Our discussion includes a presentation of the first scanning near-field optical microscopy images obtained with a free electron laser infrared sources and data on small and microscopic-scale fluctuations of semiconductor interface barriers.

11:00am **SS3+AS+NS-ThM9 Imaging and Charge Transport Measurements using Dual-Probe Scanning Tunneling Microscopy***, **H. Grube**, J.J. Boland,* University of North Carolina

Scanning tunneling microscopy has evolved into a valuable tool for the study of semiconductor and metal surfaces. However, the single probe geometry of STM limits its application to local and static measurements of the local density of states.@footnote 1@ Incorporation of a second electrically and mechanically independent STM tip within nanometers of the first enables measurements of surface properties that conventional STM cannot perform.@footnote 2,3,4@ Our DP-STM has been characterized by placing both tips in close proximity on a sample surface and obtaining images from each tip showing its local surface environment and the other probe. We discuss the challenges encountered of DPSTM and the feasibility of charge transport measurements on a variety of systems including carbon nanotubes. @FootnoteText@ @footnote 1@ G. Binnig et al., Phys. Rev. Lett., 49 (1), 57 (1982)@footnote 2@ Q. Niu, M. C. Chang and C. K. Shih, Phys. Rev., B 51 (8), 5502 (1995)@footnote 3@ J. M. Beyers and M. E. Flatte, Phys. Rev. Lett., 74 (2), 306 (1995)@footnote 4@ J. M. Beyers and M. E. Flatte, J. Phys. Chem. Solids., 56 (12), 1701 (1995)

11:20am **SS3+AS+NS-ThM10 The Miniature Cylindrical Mirror Analyzer: A New Tool For Surface Analysis***, **K. Grzelakowski**,* Focus Polska Sp. Z o.o., Poland*; M.S. Altman,* Hong Kong University of Science and Technology, P.R. China

The design and performance of a new miniature cylindrical mirror analyzer (CMA) are presented. The CMA comprises outer and inner cylinders, integral on-axis electron gun, and detector system consisting of ring aperture and channeltron, all mounted on a 2.75" flange. Entrance angle, sample-to-detector distance, and polar cone angle were chosen, in consideration of second order focussing effects, that optimized analyzer transparency and resolution. Fringe field correction at the ends of the CMA is made by means of six rings precisely separated by sapphire insulators. The electron gun is a one-lens electrostatic system equipped with XY-deflector for beam adjustment and scanning. A CeB6 low temperature cathode operating at up to -2.0keV delivers emission current up to 100 mA. The energy range of analyzed electrons can be varied between 0 eV to 2.0 keV. The flange mounting also incorporates a high precision Z-motion for optimization of the working distance. The control electronics and software permit operation of the instrument in pulse and phase sensitive detection modes. Results obtained for a W(001) surface with this new miniature CMA demonstrate an energy resolution of 0.08%, which is comparable to larger 6" and 8" flange mounted instruments. The very small size of the mini-CMA permits its use in small or crowded ultra high vacuum chambers or where only 2.75" ports are available, thereby increasing flexibility in surface analysis.

11:40am **SS3+AS+NS-ThM11 Investigations of Surface Reactions on Thin Film-Supported Catalysts Using Microhotplate Arrays***, R. Walton, R. Cavicchi, **S. Semancik**, M. Class, J. Allen, J. Suehle,* National Institute of Standards and Technology

This presentation describes the use of microhotplate arrays and electrical measurements for efficiently investigating surface reactions on supported metal catalysts under varied temperature and gas exposure conditions. Each ~100 µm x 100 µm microhotplate platform used in our work includes functionality for rapid control and measurement of film temperature (thermal time constant ~ 1 ms) and for probing of gas-induced changes in a film's electrical properties. Arrays of individually addressable microhotplates are well suited for directly comparing catalytic layers of different composition, loading, and degree of dispersion. The results we present are relevant to both gas sensing and catalysis. Specifically, four-element arrays were used to evaluate reactions on Pt, Pd, and Cu catalyst particles (formed by annealing 25-100 Å layers) supported on tin oxide. Electrical conductivity was used to monitor changes in the electron density of the thin film catalysts caused by surface reactions in air of H@sub 2@, CO and CH@sub 3@OH, respectively, at film temperatures ranging from 20 to 500 °C. Each of the catalysts interacts with these reactants in air to produce changes in film conductivity that we relate to factors including surface oxygen concentration, reaction rates, catalyst loading, and catalyst fouling. As a further example of this approach, we also illustrate the use of microhotplates to explore the conditions of thermal cycling and partial pressures under which CO oxidation oscillations occur on Pt particles supported on SnO@sub 2@.

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[1] **Morton S. Traum Award Finalist**

Thursday Afternoon, October 28, 1999

Applied Surface Science Division
Room 6A - Session AS-ThA

Polymer Surfaces, Films, and Interfaces

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

2:00pm **AS-ThA1 Conformation and Orientation Effects in the XPS Spectra of Thin Polymer Films***, **G. Beamson**,* Daresbury Laboratory, U.K., United Kingdom **INVITED**

The conformation and orientation of polymer chains at surfaces and in thin films can play an important role in determining the properties of technological systems, and may be different from the bulk polymer. Techniques such as GIXS, NEXAFS, AFM, infrared spectroscopy, ellipsometry and XPS are currently being used to investigate the arrangement of polymer chains at surfaces. Conformational effects in the XPS spectra of polymers are small, but advances in instrumentation over the past decade have increased their probability of detection. The search for conformational signatures requires careful measurements on well characterised polymers as a function of conformational change. Changes in conformation often accompany a change in crystallinity or physical state. Polymers suffer x-ray induced degradation during XPS which can mask subtle conformational effects. Hence time dependent studies are required to establish upper limits on x-ray exposure times such that degradation is not a concern. Differential charging can also mask subtle spectroscopic effects and good charge compensation is crucial for the detection of conformational signatures. Orientation effects in polymer systems can be probed by angle dependent XPS studies. A conformational signature in the C 1s spectrum of PET will be discussed and comparison of XPS and infrared data will be used to demonstrate faster conformational change at the surface than in the bulk when the polymer is annealed above Tg. Conformational signatures in the valence bands of PEG, PTMG and nylon 12 will also be described. Angle dependent XPS studies of orientation effects in molecular overlayers on PTFE tribological transfer films will be discussed. Functional group orientation effects in acrylic polymers will also be described.

2:40pm **AS-ThA3 Correlative XPS and FTIR Imaging Analysis of Polymer Blends***, **J.E. Fulghum**, K. Artyushkova, A.C. Ferryman,* Kent State University*; J.L. Koenig,* Case Western Reserve University

Phase segregation in blends of poly(vinyl chloride) and poly(methyl methacrylate) has been evaluated through correlation of photoelectron and infra-red images and small area spectra. Polymer surfaces which are heterogeneous on the scale of microns can be characterized by XPS if both imaging and small area spectroscopy are utilized. Polymer compositions in the bulk phase are routinely evaluated using FTIR spectroscopy. In this study, we take advantage of recent advances in the imaging capabilities of both techniques to improve characterization of heterogeneous organic samples. Surface-specific chemical information was acquired using a Kratos AXIS Ultra photoelectron spectrometer, while phase-segregation in the bulk was studied using a Biorad Stingray FTIR microscope. Images of comparable spatial resolution are readily obtained, allowing for a more complete characterization of lateral and vertical phase segregation than is possible with a single spectroscopic technique. Core and valence band XPS determinations of polymer blend composition in phase-separated regions will be compared to results based on small-area FTIR spectra. This work has been partially supported by NSF DMR89-20147 and 3M.

3:00pm **AS-ThA4 Beam Induced Damage Effects in XPS Studies of Thin Organic Films***, **H. Cohen**, R. Maoz, E. Frydman, J. Sagiv,* The Weizmann Inst. of Science, Israel

Beam induced irreversible effects are frequently overlooked in XPS studies of thin organic films, mainly because of limitations in self testing capabilities of the technique. Minimization of such effects requires elaborated experimental procedures, and a fundamental understanding of the dominant damage mechanisms. Aiming at this goal, a thorough study of X-ray induced effects in layered self assembled organic films has been conducted using a number of complementary techniques, additional to the in-situ XPS measurements. Chemical functions particularly sensitive to the X-ray radiation have been identified. Structural and chemical modifications are discussed as a function of the initial film composition, and their significance for potential applications is indicated.

3:20pm **AS-ThA5 Surface Analysis of Nitrogen Plasma-Treated Poly (ethylene-2,6-naphthalate) Films using XPS and Gas Phase Derivatization Reactions***, **Y. Liu**, L. Gerenser,* Eastman Kodak Company

Nitrogen plasma-treatment is a very useful technique for modifying the surface properties of polymers, including adhesion, wettability and biocompatibility, through the introduction of nitrogen functional groups. This presentation will focus on the characterization of nitrogen plasma-treated poly (ethylene-2,6-naphthalate) films using conventional XPS and gas phase derivatization reactions in combination with XPS. The selectivity and yield of trifluoroacetic anhydride for primary amines, and trifluorotolualdehyde for secondary amines, were determined by reacting them with model compounds containing the nitrogen group of interest (e.g., primary and secondary amines, amides and nitriles). The quantity and depth distribution of primary and secondary amines for nitrogen plasma-treated PEN were evaluated as a function of gas composition (e.g, N@sub 2@, NH@sub 3@, and N@sub 2@O) and treatment conditions (power and pressure). Correlations were found between the plasma conditions and the resultant surface chemistries.

3:40pm **AS-ThA6 Quantitative Analysis of Functional Groups with TOF-SIMS***, **T. Fladung**, D. Wolany, T. Gantenfort, L. Wiedmann, A. Benninghoven,* Universität Münster, Germany

The unique identification and quantitative analysis of functional groups from plasma treated polymer surfaces with XPS and TOF-SIMS is often difficult. In this case, derivatization and subsequent quantitative XPS is well-known for a number of important functionalities. We will show that the analysis of derivatization products with TOF-SIMS can extend the limited sensitivity of XPS by several orders of magnitude and, at the same time, be made quantitative by suitable calibration. After gas phase derivatization of hydroxide groups with trifluoroacetic anhydride (TFAA), the XPS results of monofunctional model polymers can be used as standards for the calibration of SIMS data. During TOF-SIMS analysis of the model polymers after derivatization, the intensity of a characteristic set of molecular ions containing fluorine is proportional to the concentration of OH groups as determined by XPS, and can thus be taken as a quantitative measure of the surface concentration of OH groups. For polypropylene and polycarbonate samples treated in an oxygen and argon plasma, respectively, the modified surfaces were derivatized with TFAA and analyzed with XPS and TOF-SIMS. The results were used to quantitatively distinguish the OH groups from other functionalities generated by the plasma such as carbonyl or carboxyl groups. Principal component analysis was used for the comparison of SIMS spectra before and after derivatization. This seems to be a promising way to establish a direct assignment of secondary ions to specific functional groups. In this way the quantitative chemical analysis of surface functionalities by TOF-SIMS should become possible without derivatization.

4:00pm **AS-ThA7 Determination of Helical Conformation Effects in PTFE NEXAFS Spectra with FEFF8 Calculations***, **D.G. Castner**, L. Gamble,* University of Washington*; D.A. Fischer, B. Ravel,* National Institute of Standards and Technology

Near edge X-ray absorption fine structure (NEXAFS) experiments can provide information about the orientation of adsorbed small molecules, self-assembled monolayers and polymers. Long fluorocarbon chains are known to have a twisted (or helical) structure due to the steric interactions of the fluorine atoms. FEFF8 calculations of the C K-edge and F K-edge spectra of poly(tetrafluoroethylene) (PTFE) have been done to determine how changing the helical structure of the PTFE chains affects the NEXAFS spectra. Experimental NEXAFS spectra were obtained at beamline U7A of the NSLS on highly-oriented PTFE samples prepared by rubbing a block of PTFE across a gold-coated silicon wafer heated to 150°C. The helical chains in this well-ordered film are oriented parallel to the gold surface and along the rubbing direction. A large polarization dependence is observed at the F K-edge for the C-F @sigma@* peak and at the C K-edge for the C-F @sigma@* peaks (at 292.6eV and 299eV) and the C-C @sigma@* peak at (296.4eV). FEFF8 NEXAFS spectra calculated with self-consistent spherical muffin-tin potentials, a full multiple-scattering formalism, the structural coordinates for bulk PTFE, and no adjustable physical parameters are in good agreement with the experimental NEXAFS spectra. Variation of the F-C-F bond angle in the calcuated spectra showed that when this angle is commensurate with the helicity of the chains, F atoms from adjacent CF2 groups become aligned in the axial direction. This alignment results in a large change in the NEXAFS spectra. Calculations that varied the radial distance of the carbon atom from the molecular axis showed that a "straight" backbone produces significantly different NEXAFS spectra than a helical backbone. Further calculations show that "stretching" and "compressing" the helical chain can also effect the widths, positions, and intensities of peaks in the NEXAFS spectra.

4:20pm **AS-ThA8 Monitoring the Kinetics of Migration/ Absorption/ Desorption/ and Cross-linking in a Curing Silicone Coating, using the QCM-D Technique***, P. Dahlqvist,* Q-Sense AB, Sweden*; **M. Rodahl,*** Chalmers, Sweden*; P. Bjoorn,* Q-Sense AB, Sweden*; M. Berglin, P. Gatenholm,* Chalmers, Sweden

The Quartz Crystal Microbalance - Dissipation (QCM-D) technique allows real time measurements of properties and processes in nm-um thin polymer and bio-films (M.Rodahl et al., Faraday Discuss. 107, 229 (1997)). Via changes in the resonant frequency, f, small mass changes (ng/cm2) are measured. Via changes in the energy dissipation factor, D, energy losses due to internal and interfacial friction in the polymer film are measured. This makes the technique a versatile tool to, e.g., phase transitions and polymerisation kinetics. In this work we studied the cross-linking kinetics of approximately 0.5 um thick films of silicone (PDMS) in the presence of various concentrations of catalyst and cross-linker (Tridecafluoro - 1,1,2,2, - tetrahydro - octyl triethoxysilane) (FTEOS), at varying humidity. The fluorine-rich FTEOS migrates to the surface due to phase separation and due to minimisation of the systems surface energy. The kinetics of the migration has been monitored and found rapid, most of the migration take place in the first 15 minutes. Water adsorption and ethanol desorption were monitored over time. The water absorption is dominant in the start of the reaction, but after a few minutes to hours, depending on relative humidity, catalyst and FTEOS concentration, the ethanol desorption becomes dominant. The cross-linking rate monitored with the dissipation factor, is highest in the beginning and slowed after 0.5 - 5 hours, depending on relative humidity and catalyst concentration.

4:40pm **AS-ThA9 Angle Resolved XPS Study of Random Fluoro-methacrylate Copolymers***, **W.E. Kosik**, S.H. McKnight, J.M. Deitzel, N.C. Beck Tan,* Army Research Laboratory

Design and control of polymer surface functionality is desirable for numerous applications. It is widely known that hydrophobic polymer surfaces can be produced on block-copolymers due to surface segregation of hydrophobic blocks, including flouro and siloxane species. Less research has been performed on random copolymer compositions. In this work, we investigate the surface segregation of a random copolymer of polymethylmethacrylate (PMMA) and tetrahyrdorperflouroctyl acrylate (PTAN). Copolymers containing different ratios of the two repeat units were examined. Thin films (150-200 nm) were solution spun-cast onto silicon substrates. As-deposited and samples annealed above the copolymer glass transition temperature were studied to assess the degree of surface reorganization that might occur. Angle resolved XPS was used to study the fluorine content of the thin films as a function of depth. It was observed that the concentration of fluoro groups increases near the surface of the film in all compositions. The degree of surface segregation was dependent on the PTAN to PMMA ratio of each copolymer. Furthermore, the segregation was enhanced after annealing of the films at elevated temperatures. Water contact angle measurements were in agreement with the angle resolved XPS results. Potential applications of these materials for selectively permeable membranes are discussed.

5:00pm **AS-ThA10 Surface Analysis Characterization of Titanium/Sol-Gel/Polyimide Adhesive Systems***, **J.T. Cherian,*** Boeing Materials Technology & University of Washington*; D.G. Castner,* University of Washington

Bonded titanium alloys are being evaluated for use at an operating temperature of 175°C. Determining the locus of failure for bonded titanium lap-shear specimens is part of a larger effort to develop durable, environmentally safe surface treatments for titanium alloys. Surface-treated titanium alloy (Ti-6Al-4V, Ti3Al-2.5V, and Ti15V-3Al-3Cr-3Sn) plates are bonded in a standard lap-shear specimen configuration and exposed to temperature for specified intervals. The lap-shear bond joint consists of two etched titanium panels that are coated with a silicon and zirconium containing sol-gel, primed with a polyimide, and then bonded together with adhesive and supporting scrim material. The lap-shear specimens are tested for overall strength and failure modes. Specimens with cohesive failure modes were examined with ESCA and ToF SIMS to determine the composition of the bond joint failure layer. Although the failure was located closer to the sol-gel/polyimide interface than to the Ti/sol-gel interface, ESCA and ToF SIMS analysis revealed that the actual location (sol-gel, primer, etc.) of the failure varies from spot to spot across a given specimen. SEM analysis suggests that the rough surface of the titanium oxide introduces stress at the interface and promotes the non-uniformity of the failure regimes. A model system is being used to investigate the interfacial bonding chemistry between the sol-gel and the polyimide primer. Pure titanium is deposited onto silicon wafers to create a smooth titanium substrate. Smooth, thin layers of sol-gel and polyimide coatings are then spun onto the Ti surface. AFM is used to measure the surface roughness of each layer. ESCA analysis in conjunction with pentafluorobenzaldehyde derivatization is used to follow the changes in the bonding chemistry at the sol-gel/polyimide interface as the sample is cured.

Friday Morning, October 29, 1999

Applied Surface Science Division
Room 6A - Session AS-FrM

New or Improved Surface Related Analytical Techniques

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

8:20am **AS-FrM1 LEIS Measurement of Target Mass in the Presence of Inelastic Energy Losses@footnote 1@***, **R. Bastasz**, J.A. Whaley,* Sandia National Laboratories

Low-energy ion scattering (LEIS) is often used to identify the elements present on a surface. Peaks observed in the energy spectrum of scattered ions can be assigned to specific target masses. However, the usual kinematic expression that relates the energy of a scattered projectile to a target atom mass does not account for inelastic losses, such as ion neutralization/reionization and excited state formation, which can significantly affect the scattered-ion energy. We have developed a simple method for unambiguously determining target atom mass from LEIS measurements regardless of the amount of inelasticity in the collision. Analysis of the scattering kinematics with an included inelastic loss term shows that the scattered particle velocities form a circle in the polar coordinate system (v@sub n@,@theta@), where v@sub n@ is the normalized scattered-ion final velocity and @theta@ is the laboratory scattering angle. While the circle radius changes with the degree of inelasticity, the circle center depends only on the target-to-projectile mass ratio. So, by measuring ion energy spectra at three or more scattering angles, it is possible to construct the appropriate scattering circle, find its center, and deduce the target mass. The only assumption in the method is that inelastic losses are not a function of the impact parameter. This assumption appears reasonable at typical observation angles, as can be illustrated with several examples of inert-gas scattering from low-Z metal surfaces. @FootnoteText@ @footnote 1@ This work was supported by the US Department of Energy under contract DE-AC04-94AL85000.

8:40am **AS-FrM2 Atmospheric Electron X-ray Spectrometer***, **J. Feldman**, J.Z. Wilcox, T. George,* Jet Propulsion Laboratory*; D.N. Barsic, A. Scherer, T. Doll,* Caltech

Atmospheric Electron X-Ray Spectrometer (AEXS) J. Feldman, J. Z. Wilcox, and T. George, Jet Propulsion Laboratory D. N. Barsic, T. Doll, and A. Scherer, Electrical Engineering and Applied Physics, Caltech Abstract The Atmospheric Electron X-ray Spectrometer (AEXS) is a new miniature instrument being developed for in situ elemental analysis of surfaces. The key component of the instrument is a microfabricated silicon nitride membrane. This electron transmissive membrane serves to isolate the high-vacuum electron column from the ambient atmosphere. An electron beam generated and focused in the column is transmitted through the membrane to impinge on the sample in the ambient atmosphere. The electron beam excites characteristic x-rays, which are analyzed to determine the elemental composition of the irradiated portion of the sample. The power of this type of analysis is that samples can be analyzed in situ without being introduced into a vacuum chamber as in traditional scanning electron microscopy (SEM). Due to the return ionization path through the atmosphere, sample preparation is unnecessary even for non-conductive samples. This talk describes the development and current status of the AEXS. Initial spectra were obtained in ambient Earth atmosphere with a spot size of less than 1mm and a spectrum acquisition time of a few minutes. The physical properties of a number of candidate low atomic number microfabricated membranes, including electron and x-ray transmissivity, will be discussed. The prototype instrument is designed to be portable, with a mass of 1 kg. The high spatial resolution of the AEXS (as compared to alpha particle or x-ray fluorescence instruments) will enable mapping of compositional heterogeneities at a grain size level. In addition to applications in planetary exploration, the AEXS also has potential applications in industrial process monitoring and quality control.

9:00am **AS-FrM3 Advances in X-ray Photoemission Spectroscopy at Very High Spatial and Spectral Resolution***, **B.P. Tonner**, R. Kneedler,* University of Central Florida*; K. Pecher,* California Institute of Technology*; T. Warwick,* Lawrence Berkeley National Laboratory **INVITED**

Soft x-ray undulator synchrotron radiation has resulted in dramatic improvements in the performance of x-ray photoemission spectroscopy (XPS)for the study of surfaces and shallow interfaces. The two main areas of improvement are in spatial resolution and spectral resolution, which, in combination, result in improved sensitivity of the technique. Recent work with complex surfaces, such as the surfaces of natural minerals, will be used to show that fundamental issues regarding surface composition of such materials can be resolved using XPS imaging and spectroscopy from sub-micron areas. XPS microscopy is used to qualify surfaces for further analysis using high resolution photoelectron diffraction (XPD). XPD studies of large unit cell surfaces, and of mineral surfaces, will be selected to illustrate the precision of atomic geometry that can be determined. Examples will be drawn primarily from our work on copper sulfide, bixbyite, galena, and pyrite surfaces.

9:40am **AS-FrM5 An Evaluation of the ALS Micro-ESCA Beam Line Performance for Small Particle Analysis***, **C.R. Brundle**, Y. Uritsky, G. Conti,* Applied Materials, Inc.*; P. Kinney,* MicroTherm, LLC*; Y. Ynzunza,* Intel Corporation*; E. Principe,* Charles Evans and Associates

Intel, Applied Materials, and the ALS synchrotron staff have developed a micro-ESCA beam line at the Advanced Light Source, LBL. One of the major objectives was to produce "user-friendly" analysis at a spatial resolution significantly beyond that available in commercial instrumentation. We review the status of the project using both test structures and real particle situations and conclude the following: 1) Usable signal intensities are attainable down to ~2 µm size features, the nominal X-Ray beam size. This is 5 to 10x better than the PHI Quantum 2000. 2) The sample handling and navigation system to find small features works well (considerably better than any commercially available approach on ESCA systems). 3) The availability of the NEXAFS operation mode, in addition to the ESCA mode, provides valuable additional chemical state delineation capabilities. 4) Charging issues for insulating films and particles need to be resolved. 5) Since the "turn-around" analytical time and spatial resolution will always be far worse than for commercial SAM, the practical usefulness of the beam line depends strongly on its enhanced capability, compared to SAM, for chemical state delineation using the ESCA chemical shifts and near-edge structure, and on the reduced beam effects compared to e-beam SAM.

10:00am **AS-FrM6 A Study of TOF-SIMS for the Analysis of Metal Contamination on Silicon Wafers***, **I.A. Mowat**, T.J. Schuerlein, J. Metz, R. Brigham, D. Huffaker,* Charles Evans & Associates

The current methods of choice for the analysis of metal contaminants on silicon wafers are Total Reflection X-Ray Fluorescence (TXRF) and SurfaceSIMS. TXRF is a survey technique, with good detection limits for transition metals (e.g. down to 10@super 9@atoms/cm@super 2@ for some elements). SurfaceSIMS is not usually used as a survey technique, but it has high sensitivity for species such aluminum and alkali metals (species not detected well by TXRF). Time-of-flight SIMS (TOF-SIMS) is a technique which offers a surface survey of all metal contaminants, with good detection limits. This paper details the investigation of TOF-SIMS as a possible tool for such analyses. Under the high beam current conditions used, elemental information is obtained with high sensitivity (under certain conditions, the detection limit for iron can be below 10@super 9@atoms/cm@super 2@, and is much lower for the alkali metals). Experiments were carried out to investigate the accuracy and precision of TOF-SIMS analyses of Si wafers. The areas of interest were: (1) short term variability of data from a standard spin coated wafer; (2) long term variability (over approximately six months) of data from the same wafer; (3) investigation of factors affecting the detection limits achievable by TOF-SIMS; (4) cross correlation of TOF-SIMS with established techniques such as TXRF and SurfaceSIMS. Short term variability was determined to be in the range 10-12%, and long term variability was ~20%. Work is underway to investigate the sources of this variability. Detection limits were studied by assessing wafers from different sources in the semiconductor industry, and were found to vary by up to a factor of five. Cross correlation with both TXRF and SurfaceSIMS have proven to be a good source of information to increase the accuracy of TOF-SIMS measurements. The information obtained will help assess the suitability of TOF-SIMS as an additional method for metal contamination measurement on silicon wafers.

10:20am **AS-FrM7 Fundamental Studies of Polymer and Protein Cationization by ToF-SIMS***, **R Michel**, R. Luginbuehl, D.J. Graham, B.D. Ratner,* University of Washington

Cationization of polymers, proteins and polypeptides is carried out on novel substrates with Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). The surfaces consist of carboxylic terminated self-assembled monolayers with various metal ions such as Ag, Na, Li, Tl, and Cu substituting the terminal hydrogen. The resulting surfaces are used as carrier substrates for deposition and analysis of polymers, proteins and polypeptides. Low (1 kD) and high (400 kD) molecular weight polyethyleneoxide (PEO) was deposited via spincoating while the proteins were adsorbed to the substrates. Previously published results show that cationization of polymers was achieved with the various selected metal ions from the carboxylic terminated groups. Complementary experiments carried out on non-substituted and methyl terminated self-assembled monolayers suggested that metal ions which are desorbed from the gold surface and therefore not in close proximity to the polymer do not cationize polymers and their fragments. The intensity of the cationized fragments were observed to be dependent on the metal ion used. Both cationized fragments and whole molecular species were observed for the 1kD PEO while on 400 kD PEO chain fragments of up n = 25 monomer units were detected. For protein samples using our substrate, detection of whole low molecular weight proteins up to 2 kD could be achieved with additional peak patterns indicating a loss of peptide- and sidechains.

10:40am **AS-FrM8 Synchrotron TXRF Quantification Using Ion Implanted Standards***, R.L. Opila,* ***J.P. Chang****, J. Eng, Jr., J.R. Rosamilia,* Bell Labs, Lucent Technologies*; P. Pianetta,* Stanford University*; F.A. Stevie, R.F. Roberts, M.A. Decker,* Bell Labs, Lucent Technologies

Much of the difficulty in quantification using TXRF has been associated with problems in obtaining suitable standards. The quantification can be very accurate, but the standards to date are difficult to prepare and are not generally available. Ion implantation is often used for quantification of secondary ion mass spectrometry and can be obtained for any element, but the implanted distribution is not well defined at the surface. The technique of implantation through a sacrificial oxide layer has been applied to create TXRF quantification standards. Ion implants of Ca, Fe, Cu, Ni, As, and Sb were made through 0.1 µmm SiO@sub 2@ on Si substrates. Measurements were made using conventional and synchrotron TXRF after removal of the oxide. The results show that there is a direct correlation between the ion dose and the TXRF measured dose in the sampling depth for TXRF. Measurements were made using surface and time-of-flight SIMS, with similar conclusions. Certain elements, e.g., copper, are known to plate on the surface after oxide etch. One unique advantage of performing TXRF at the synchrotron is the ability to easily change the energy of the exciting x-rays. Using the dependence upon incident photon energy it is possible to collect a near edge absorption spectrum of the metallic species. This near edge spectrum then permits determination of the chemical bonding of the metallic element. By varying the angle of the incident x-rays above and below the critical angle, the difference in states between an impurity at the surface versus an impurity in the bulk can be determined. If metal remains on the surface, as suggested by the copper data, the surface copper can be removed. This removal was verified using synchrotron TXRF, XPS, and TOF-SIMS.

11:00am **AS-FrM9 A Comparative Evaluation of FIB CVD Processes***,* ***B.I. Prenitzer****, B.W. Kempshall, L.A. Giannuzzi,* University of Central Florida*; S.X. Da,* FEI Company*; F.A. Stevie,* Cirent Semiconductor (Lucent Technologies)

The metal chemical vapor deposition (CVD) capability available in focused ion beam (FIB) instruments has found multiple applications, e.g., in semiconductor device modification, for mask repair, and as a means to protect the region of interest during specimen preparation for electron microscopy. Added versatility has been afforded to CVD processes by the introduction of the dual beam FIBs. Dual beam instruments incorporate both an electron column and an ion column into a single FIB, and therefore allow the CVD process to be either ion or electron assisted. Evidence indicates that the mode of deposition may be significant in determining the final properties of the metal line, i.e., chemical composition and resistivity. In addition to the characteristics of the metal line itself, damage has been observed in the surface layers of specimens in which ion beam assisted CVD processes have been employed. Maintaining the integrity of the surface layers is particularly critical when preparing specimens for subsequent microstructural and/or microanalytical evaluation of ultra-shallow regions. Cross-section transmission electron microscopy (TEM) is used to evaluate the surface integrity of single crystal Si substrates on which Pt metal lines have been grown by ion and electron beam assisted CVD processes. The effectiveness of various surface coatings in the prevention of radiation damage during ion beam induced CVD is also investigated.

11:20am **AS-FrM10 High Resolution Sum Frequency Generation of a Rubbed Octadecyltriethoxysilane Self Assembled Monolayer on Glass***,* ***T.E. Furtak****, B.C. Chow,* Colorado School of Mines

Over the last decade, optical sum-frequency generation(SFG) has made the acquisition of vibrational spectra of surface species possible. However, the SFG instrumentation that has usually been employed suffers from low spectral resolution due to the use of band-width-limited picosecond lasers. Using a nanosecond source, we have been able to achieve a resolution nearly two orders of magnitude better than that characterized by a picosecond source. Exploiting this advantage we have observed previously unresolved features in the vibrational spectra of rubbed self-assembled monolayers of octadecyltriethoxysilane(OTE) on glass. We have been able to establish a relationship between the effect which rubbing produces and the surface coverage of the molecule through the ratio of the chain -CH@sub 2@- and terminal -CH@sub 3@ features in the spectrum. This new insight will be of value to surface modification technologies, particularly those involving liquid crystal displays.

11:40am **AS-FrM11 The Use of Field Ionization Methods to Probe the Influence of High Interfacial Electric Fields on Electrochemical Phenomena***,* ***V.K. Medvedev****,* University of Washington*; D.L. Scovell,* University of Washington, U.S.A*; C.J. Rothfuss, E.M. Stuve,* University of Washington

One characteristic of the electrode/electrolyte interface is the presence of high electric fields, typically on the order of 1 V/Å. With sharp field emitter tips, sufficiently high electric fields can be generated at the tip surface by application of a few kV bias potential. We have developed a field ionization microscopy and mass spectroscopy system for studying the influence of high electric fields on ionization of water. Water is adsorbed on a platinum field emitter ⍰adius 350 Å under both field-free and applied field conditions. Water adlayers ranging in thickness from 0 to 5000 Å have been examined at temperatures ranging from 30-300 K at pressures below 10@super -6@ torr. Water ionization was detected by time-of-flight and Wien filter (ExB) mass spectroscopies and imaged on a phosphor screen. Experimental and numerical results to date show that: (1) fields of only 0.2-0.5 V/Å can increase the ionic content of the water layer by several orders of magnitude; (2) the ions formed are hydrated by as many as 10 water molecules; (3) the onset of water ionization on a clean Pt tip increases linearly with temperature over the range of 170-300 K; and (4) ions formed at the tip/water interface must diffuse through the water layer prior to detection. The distribution (n) of (H@sub 2@O)@sub n@H@super +@ clusters is a strong function of ionization conditions and provides information on the nature of surface diffusion as a function of temperature. The diffusional barrier for ion transport through the water layer appears to be a function of applied electric field and the nature (amorphous vs. crystalline) of the water layer.

Surface Science Division

Room 606 - Session SS1+AS+BI-FrM

Organic Films/Self-Assembled Monolayers

Moderator: G.E. Poirier, National Institute of Standards and Technology

8:20am **SS1+AS+BI-FrM1 Simple Viscosity Model Analysis of Hydronium Ion Motion in Nanometer Organic Films***,* ***K. Wu****, M.J. Iedema, J.P. Cowin,* Pacific Northwest National Laboratory

Nanometer organic films such as methylcyclohexane and 3-methylpentane were vapor-deposited at 30 K on Pt(111) with a molecular beam. Pure hydronium ions were soft-landed on top of the films at a kinetic energy less than 1.2 eV. The voltage change and desorption of the organic films were simultaneously monitored by a Kelvin probe and a mass spectrometer. Ion dosing on the organic films was a capacitive charging process, therefore the film voltage change actually reflected the ion motion in the organic films, assuming the dielectric constants of the organic films do not change much with temperature. When the films were warmed, ions gradually moved into the films. The experimental results were analyzed by a simple viscosity model. To a large extent, the temperature (or time) evolution of the film voltage could be well predicted by the model. The film voltage fall-off temperature width from the theory was, however, about half of that from the experiment. Further experimental evidence showed that the ion self-generated electric field strength had a strong effect on the ion motion. For example, when the electric field strength was higher than 0.05 V/Angstrom, the theoretical prediction seriously deviated from the experimental result, indicating that a high electric field might trigger non-linear ion motion and made the Stokes-Einstein equation not accurate. When films were prepared at higher temperatures, methylcyclohexane could crystallize on Pt(111), making ions more difficult to transport in the crystalline films. But, 3-methylpentane never crystallized before ion motion in it completed, indicating that it's a good glass material. With this general approach, we could attack many important issues such as ion motion across liquid-liquid interfaces, hydration of ions and so on.

8:40am **SS1+AS+BI-FrM2 Direct Observation of Topological Defect Evolution and Domain Motion in Ultrathin Films of PS-b-PMMA Diblock Copolymers Using Atomic Force Microscopy***, **J. Hahm**[1], W.A. Lopes, H.M. Jaeger, S.J. Sibener,* The University of Chicago

We report the tracking of individual topological defects in the microdomain patterns of cylinder-forming polystyrene-block-polymethylmethacrylate (PS-b-PMMA) films. These films undergo vertical and lateral phase separation when they are thermally annealed. The vertical phase separation results in thickness quantization where each layer exhibits its own topology and dynamics. The lateral phase separation provides height contrast between the two components of the diblock in single-cylinder-layer thick films. In the atomic force microscopy (AFM) topographic images, the PMMA is higher by approximately 1nm as compared to the PS blocks. 50nm thick films, containing a single layer of cylinders aligned parallel to the film plane, were repeatedly and non-destructively probed with AFM in an attempt to elucidate the evolution of the diblock domain topology between annealing treatments. We show explicitly that the evolution of topological defects takes place through relinking, joining, clustering and annihilation of defects. Such processes form the basis for predicting structural changes in polymer thin films. We also have used time-lapse AFM imaging to observe directly the kinetics of domain mobility responsible for topological evolution. Domains of different thicknesses were monitored as a function of annealing temperature and time. The higher mobility and lower activation energy associated with thicker domain mobility are accounted for by the essentially negligible substrate interactions where polymer-polymer rather than polymer-substrate interactions govern the dynamics. Our hope is that the combined understanding of topological changes, such as those reported in this talk,when combined with mobility kinetics, will give us a predictive understanding of the thermally activated structural changes that occur within thin polymer films. @FootnoteText@ Supported by the NSF-MRSEC at the University of Chicago and AFOSR.

9:00am **SS1+AS+BI-FrM3 Properties of Self-Assembled Monolayers of Biphenyl-Based Thiols***, **T. Felgenhauer**, H.-T. Rong, M. Buck, M. Grunze,* University of Heidelberg, Germany

Despite their versatility to modify surface properties, self-assembled monolayers (SAM) based on alkane thiols have limitations concerning conformational stability or structural perfection. In search for more rigid molecules, thiols based on aromatic moieties offer an alternative. However, in contrast to SAMs consisting of alkane thiols experiments on aromatic thiols are relatively scarce. Our experiments focus on thiol SAMs consisting of 4,4'-substituted biphenyls (BP). To allow systematic investigations the number of methylene units between the biphenyl moiety and the thiol group was varied between zero and six. The electrochemical behavior of BP-SAMs turns out to be very different from alkane thiols. In general, the charge permeability of BP-SAMs is higher by orders of magnitude even though the electrochemical stability of BP-SAMs is dependent on the methylene spacer. Exposure to an etching solution reveals a stability significantly higher compared to alkane thiols and suggests an improved structural perfection of BP-SAMs. Spectroscopic characterization of the BP-SAMs yields an orientation of the biphenyl units alternating with the methylene chain length. Comparison of BP-SAMs on Au with those on Ag shows a reversal of the odd-even effect and demonstrates that the sulphur-substrate bond is crucial for the molecular orientation of the biphenyl-SAMs.

9:20am **SS1+AS+BI-FrM4 Structure of Self-assembled Monolayers of Alkanethiols and Disulfides on Au(111)***, **H. Nozoye**,* National Institute of Materials and Chemical Research, Japan*; C. Kodama, T. Hayashi,* University of Tsukuba, Japan

Self-assembled monolayer (SAM) films of alkanethiols and alkyldisulfides have been attracting an increasing interest. However, we do not have a concrete picture of SAM, e.g. is the SH bond broken on the surface ? , is the SS bond formed on the surface ?, or where is the adsorption site of S ?. We studied these problems by means of STM, HREELS, high-sensitivity LEED, and TPD. Alkanethiols (C1-C10) and alkyldisulfides (C2-C12) were adsorbed on a Au(111) single crystal surface at room temperature or at around 120 K. Dersorption of H2, parent alkanethiol, alkylthiolate radical, and alkyldisulfide were observed in TPD and a vibration peak assigned to a SS bond was missing in HREEL spectra. We clearly concluded that the SH bond of alkylthiols breaks at low temperature forming alkylthiolates on the surface. Furthermore, the SS bond of alkyldisulfides was shown to be broken on the surface, forming alkylthiolate. The Au-S bond of alkylthiolates on the surface gave a relatively strong peak in HREEL spectra. We will discuss the formation process and the relation between the local structure and the long-range order of SAM.

9:40am **SS1+AS+BI-FrM5 Toward Vapor Deposition of Polycyanurates: The Surface Chemistry of Phenyl Cyanate and Phenol on Al(111)***, B. Bartlett, J.M. Valdisera, **J.N. Russell, Jr.**,* Naval Research Laboratory

Polycyanurates, formed by polymerization of monomers containing two cyanate groups, show promise as vapor depositable, low dielectric parameter materials for microelectronics applications. Consequently, we are examining the chemistry of a model system, phenyl cyanate on Al(111) surface, with temperature programmed desorption (TPD), Auger electron spectroscopy (AES), and X-ray photoelectron spectroscopy (XPS). (Aluminum was chosen as a substrate because it is used for interconnects in microelectronics.) For submonolayer coverages, XPS shows that the phenyl cyanate undergoes O-CN bond cleavage between 150 and 200 K, leaving phenoxide and cyanide groups on the surface. Benzene and hydrogen decomposition desorption products were observed at 620 K, and between 500 and 800 K, respectively. This is analogous to the reaction of phenol on Al(111). Deuterium labeling was used to determine the sequence of C-H bond scission on the phenoxy species. XPS and AES reveal the formation of aluminum oxide, nitride and carbide on the surface above ~ 400 K. After multilayer exposures, the formation of the phenyl cyanate trimer, triphenoxytriazine, was observed with XPS between 160 and 200 K. The trimerized multilayer was stable up to ~ 500 K before it decomposed. This data suggests that at high coverages, a dicyanate functionalized molecule may chemically attach to aluminum by cleavage of an O-CN bond, while the other cyanate group is available for trimerization, thus anchoring a polycyanurate film to the surface. The surface chemistry of a dicyanate functionalized molecule, 1,1-bis(diphenylcyanato)ethane, is currently under investigation to confirm this hypothesis.

10:00am **SS1+AS+BI-FrM6 Formation of Organic Layers by Cycloaddition Reactions at Germanium Surfaces***, S.W. Lee,* University of Missouri, Columbia*; J.S. Hovis, R.J. Hamers,* University of Wisconsin, Madison*; **C.M. Greenlief**,* University of Missouri, Columbia

The formation of ordered organic layers on Ge(001) substrates is explored. Ge substrates are prepared by a novel method and exposed to a variety of cyclic hydrocarbons, including cyclopentene and cyclohexene. The subsequent surface interactions are followed by a variety of surface sensitive techniques. Bonding configurations are determined by photoelectron spectroscopy and scanning tunneling microscopy. The strength of surface interactions are also monitored by temperature programmed desorption. Cyclopentene and cyclohexene react with Ge dimer bonds via a [2+2] cycloaddition reaction. This reaction generates rows of the surface complex oriented along the dimer bond direction of the Ge(001) surface, which is easily observed by scanning tunneling microscopy. Experiments using other cyclic hydrocarbons and attempts at further surface modification will be discussed.

10:20am **SS1+AS+BI-FrM7 Multilayer Phases in Self-Assembled Monolayers Based on Silane Coupling Agents***, **B.C. Bunker**, R.W. Carpick, M. Hankins, M.L. Thomas, R. Assink, M. DeBoer,* Sandia National Laboratories

Thin films prepared using silane coupling agents are used extensively to chemically modify surfaces. In micromachines, such films are used to control stiction, friction, and adhesion of moving parts. The films are commonly depicted as self-assembled monolayers, in which each silane molecule forms extensive Si-O-Si linkages to the surface and to other molecules. However, many workers report that it is difficult to produce self-assembled monolayers on a reproducible basis, especially for films having fluorinated hydrocarbon chains. In this paper, atomic force microscopy studies are used to show that irreproducible film formation is associated with the fact that silane coupling agents can self-assemble into a range of structures described in common surfactant phase diagrams. Evidence is presented suggesting that hydrocarbon and fluorocarbon silanes form lamellar and inverse micelle structures on silica and silicon nitride surfaces. In some instances, multilayer structures are produced during fabrication. Films which start out as monolayers can also reorganize into multilayer phases after deposition. Factors influencing the phases observed include surface pretreatment, the solvent, silane and water concentrations in the deposition solution, and environmental parameters such as temperature and relative humidity. Mechanisms for the evolution of the observed range of self-assembled structures vs. reaction conditions are described.

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[1] **Morton S. Traum Award Finalist**

10:40am **SS1+AS+BI-FrM8 Self-assembled Monolayers on Silicon Surfaces: The Opposite to Siloxane Chemistry***, **J.A. Mulder**, R.P. Hsung, X.-Y. Zhu,* University of Minnesota

Self-assembled monolayers (SAMs) on silicon surfaces are of interest for a number of reasons: they may be used as monolayer resists in high resolution lithography, as dielectric layers, as active components in hybrid sensor devices, as passivation and lubrication layers in MEMS, and as a new platform for biochips. SAMs on silicon are traditionally formed via siloxane chemistry on oxidized surfaces from organosilicon derivatives, such as alkyltrichlorosilane. The problems with siloxane SAMs are well known: they are difficult to prepare and suffer from poor reproducibility; the contradiction between cross-linking and close-packing is inherent; the presence of the amorphous and insulating oxide layer is not desirable in some applications. There is much incen tive to develop simple processes for the formation of stable molecular layers directly on the silicon surface. We present a novel approach which, in essence, is the opposite to the siloxane SAM process. The assembly processes are based on the reaction bet ween R-OH or R-NH2 with chlorinated silicon surfaces, leading to molecular assembly via Si-O or Si-N linkages. These reactions are not only efficient but also sufficiently versatile for the assembly of a wide variety of functional organic molecules. A par ticular advantage of this new assembly chemistry is that it is compatible with both vacuum and solution phases and can be carried out under very benign experimental conditions. We characterize these SAMs using a variety of techniques, such as multiple-int ernal reflection FTIR, X-ray photoelectron spectroscopy, contact angle measurements, and scanning probe microscopy. We address structural and stability of these SAMs and their dependence on molecular structure, such as alkyls and aromatics. We also discuss immediate and future applications.

11:00am **SS1+AS+BI-FrM9 The Photochemistry of Model Organosulfur Compounds Adsorbed on GaAs (110): Energy-Resolved Photofragment Angular Distributions***, **N. Camillone III**, K. Adib, R.M. Osgood, Jr.,* Columbia University

Self-assembled monolayers of organothiols and related compounds hold promise for use in the semiconductor industry as ultrathin electron beam resists and precursors for the growth of II-VI materials, as well as for the growth of passivating gallium sulfide films on GaAs. An understanding of the structure and photon and electron chemistry of organothiols and related compounds is relevant to the development of these technologies. We report on our studies of the photoinduced chemistry of three model organosulfur compounds, CH@sub 3@SH, (CH@sub 3@S)@sub 2@ and CH@sub 3@SCH@sub 3@, on the (110) surface of GaAs. We find that the cross sections for the photoinduced reactions of these molecules in the adsorbed monolayers follows the trend CH@sub 3@SH > CH@sub 3@SCH@sub 3@ > (CH@sub 3@S)@sub 2@. Comparison of these measurements to photoinduced chemistry in the multilayer regime gives insight into the degree to which close proximity to the semiconductor surface perturbs the photochemistry. In addition, the structure and molecular orientation of these molecules is discussed in light of the results of energy-resolved photofragment angular distributions and low energy electron diffraction measurements. The post-irradiation chemistry of the trapped photofragments will also be discussed.

Author Index

Bold page numbers indicate presenter

Author Index

Author Index