Applied Surface Science

Room: 610 - Session AS-MoM

Quantitative Surface Analysis I. Electron Spectroscopies: (Honoring the contributions of Martin Seah, NPL, and Cedric Powell, NIST)

Moderator: D. Gaspar, Pacific Northwest National Laboratory

8:00am **AS-MoM1 Quantitative Surface Analysis - Applying Thirty Years of Progress and Addressing New Analysis Needs**, ***D.R. Baer***, Pacific Northwest National Laboratory **INVITED**

Over the past thirty plus years, advances in instrumental capability, analytical approaches and the establishment of data bases have significantly improved the reliability of instrumentation and the possible accuracy of surface analysis. The significant contributions of Cedric Powell, Martin Seah along with those of many others provided the foundation for many of these advancements and served to establish many of the elements of surface analysis as it is currently practiced. From the prospective of the growth of the use of techniques such as XPS and based on the number of surface analysis systems available around the world, it is clear that use of the methods is increasing and many users are no longer experts. At the same time, many of the pioneering researchers who have made these advancements possible and who have the greatest knowledge about the techniques are at or nearing retirement age. Thus, we currently face two different but related challenges. First, we need to establish ways to efficiently transfer the important analytical knowledge to new and often less expert analysts. Second, new types of materials make additional demands on the analytical capabilities and it is important for a new generation of researchers to pick up the challenge. This talk will note some aspects of the progress and address the current challenges from the view of a nanotechnology project manager, the use of surface analysis in a DOE User facility (the Environmental Molecular Sciences Laboratory, EMSL), and from the view of a participant in two committees developing surface chemical analysis guides and standards. From the viewpoint of a project manager, it is useful to extract as much information as possible form the techniques being used. For some nanomaterials, this often requires application of multiple techniques, sophisticated analysis of some types of data and allowing the analysis of data from one method to inform the data collection and analysis of other types of data. In the EMSL we find that we are in a constant education mode teaching users about how to plan experiments, handle samples, collect and analyze data to obtain the desired information. The ASTM Committee E42 on surface analysis is currently working on a variety of consensus guides to enable new users to apply the experience of topical experts to analyze some type of samples and problems.

8:40am **AS-MoM3 Some Highlights and New Directions in Quantitative AES and XPS**, ***C.J. Powell***, National Institute of Standards and Technology **INVITED**

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) have been productive tools for a large variety of scientific and technological purposes since commercial instruments became available almost 40 years ago. Elemental identification is relatively easy but quantitative measurements (e.g., identification of chemical state, determination of chemical composition, and measurement of film thicknesses) can be more difficult. I will give a brief overview of advances that have been made to calibrate instruments, assess surface sensitivity, and account for elastic scattering of the signal electrons. NIST databases are now available that provide XPS data, inelastic mean free paths, effective attenuation lengths (EALs), and elastic-scattering cross sections.[1] A new NIST database for the Simulation of Electron Spectra for Surface Analysis (SESSA) was recently released.[1] I will describe two applications of SESSA, one to assess the distinguishability of N composition profiles in SiON films on Si by angle-resolved XPS[2] and the other to determine EALs for photoelectrons in SiO_2.[3] Small systematic differences between the SESSA results and experimental data give new insights into photoelectron excitation and transport. Finally, I will describe results from a VAMAS project to assess the magnitude of uncertainties in XPS peak intensities associated with different techniques and procedures for background subtraction.

[1] http://www.nist.gov/srd/surface.htm.

[2] C. J. Powell, W. S. M. Werner, and W. Smekal, Appl. Phys. Letters 89, 172101 (2006).

[3] C. J. Powell, W. S. M. Werner, and W. Smekal, Appl. Phys. Letters 89, 252116 (2006).

9:20am **AS-MoM5 The Bulk Ratio Method for Determining Surface Enhancement Using Auger Analysis**, ***J.D. Geller***, Geller MicroAnalytical Laboratory, Inc.

Enhanced surface layers on stainless steel are engineered to provide improved corrosion resistance and reduced surface reactivity. Stainless steel can be electropolished and chemically treated in such a way that the surface finish is improved while enhancing the chromium levels near the surface. This modification is thought to increase corrosion protection and produce less gas stream particulates for semiconductor applications. The surface analysis techniques of x-ray photoelectron (XPS) and Auger electron spectroscopy (AES) have been used for decades to characterize the effects of these treatments by observing the near surface chemistry. International standards and practices (Sematech, ASTM F-1402-92 and SEMI 2335b), for AES and others for XPS, have been written to guide the analyst on how to calibrate their instruments, as well as collect and reduce the data. The test results most often examined are the oxide depth and maximum Cr to Fe ratio. Improved standard practices are necessary to reduce the variability that is seen between instruments and between laboratories for measuring the ratios. The variability likely stems from the use of sensitivity factors that are not representative of the host instrument and the improper selection of standards. The Bulk Ratio Method is a new approach which provides the same numerical value of chromium enhancement from data collected and reduced using either relative intensities or sensitivity factors. The Bulk Ratio can be easily calculated from historical data collected on different instruments and laboratories.

9:40am **AS-MoM6 Investigation of Average Matrix Relative Sensitivity Factors in Auger Electron Spectroscopy**, ***M. Suzuki***, *K. Mamiya, N. Urushihara, N. Sanada,* ULVAC-PHI, Inc., Japan, *D.F. Paul, S. Bryan*, Physical Electronics

Auger electron spectroscopy (AES) is widely used for surface elemental analysis of the outer several nm of a material surface. Quantification is performed by converting signal intensities to elemental concentrations with relative sensitivity factors (RSF's). In practice, elemental RSF (ERSF) or atomic RSF (ARSF) tables are utilized in AES quantification. However, ISO18118:2004[1] recommends adopting an average matrix RSF (AMRSF), which includes corrections of matrix effects that are affected by elastic scattering, backscattering, inelastic mean free paths and atomic densities. In this study we calculate AMRSF's for the primary electron accelerating voltages of 3 kV, 5 kV, and 10 kV according to ISO18118 from experimentally obtained ERSF's. Comparing AMRSF's and ERSF's, there are greater differences for main group elements than for transition elements. For main group elements, AMRSF values are smaller than ERSF's for second row elements, while they inversely correlate for fifth and sixth row elements. So far, ERSF's for AES quantification have been provided as a database for primary electron energies less than 10 kV. Higher voltages, such as 20 kV or 30 kV, are in common use today in field emission AES instruments in order to achieve high spatial resolution. Thus RSF's for primary voltages higher than 10 kV are strongly desired for quantification of small areas. Therefore, we have extended AMRSF's for higher than 10 kV using Ichimura-Shimizu's backscattering factors[2] and Gryzinski's ionization cross-sections.[3] The former ones are assumed to be extrapolatable for higher than 10 kV.[4] In order to examine the validity of these calculations, experimentally obtained AMRSF's for 3 kV and 5 kV are compared with those calculated for 10 kV AMRSF's, showing good agreement. In the presentation, concentrations derived from AMRSF's will be compared with those from ERSF's for several kinds of compound materials.

[1] ISO 18118:2004, Surface chemical analysis - AES and XPS- Guide to the use of experimentally determined relative sensitivity factors for the quantitative analysis of homogeneous materials.

[2] S. Ichimura, R. Shimizu, and J. P. Langeron.

[3] M. Gryzinski, Phys. Rev. A336, 138 (1965).

[4] S. Tanuma, private communications. (to be submitted to J. Surf. Anal.).

10:20am **AS-MoM8 Quantitative Surface Chemical Microscopy**, ***J. Walton***, The University of Manchester, UK **INVITED**

X-ray photoelectron spectroscopy is widely regarded as a mature technique, with a large instrument base, not restricted to specialist laboratories. One of the reasons for this is the apparent ease of quantification compared with other surface analytical techniques, and its ability to provide chemical state information. Yet comparison of quantified data between different instruments is still problematic. A procedure will be described for determining the instrument response function for selected modes of operation to allow quantification using theoretically determined sensitivity factors, enabling transfer of results between instruments. XPS is much less frequently used in imaging mode, which was originally developed as a guide for small area analysis. However, the consequence of the acquisition of single energy images is that the aspects that make XPS spectroscopy appealing, ie ease of quantification and provision of chemical state information, are not available, since quantification requires peak area measurement after a suitable background subtraction and chemical state information is often dependent on resolution of overlapping photoelectron peaks. These limitations can be overcome by acquiring a spectrum at each pixel in an image, known as spectromicroscopy, so that the accepted processing procedures used in spectroscopy may be applied to the spectrum image data set. The acquisition of spectrum image data sets which may consists of 1000 images each containing 256 by 256 pixels presents further challenges for the analyst charged with the interpretation of thousands of spectra with low signal/noise. The use of multivariate statistical analysis to reduce the dimensionality of the data and to improve signal/noise will be demonstrated. Procedures will then be described to characterise the instrument performance in imaging mode, and to apply a modified quantification procedure to obtain atomic concentration images. Further, it will be shown that by maintaining the relationship between images and spectra so that pixels may be classified by chemistry, leads to improved curve fitting, and provides an alternative to multivariate curve resolution in visualizing physically meaningful spectra. Finally the ability to obtain spatially resolved nanostructural information will be discussed.

11:00am **AS-MoM10 Quantitative Characterization of Nb SRF Accelerator Cavity Surfaces Based on the Work of Seah and Powell**, ***M.J. Kelley***, *H. Tian,* College of William & Mary, *C.E. Reece*, Thomas Jefferson National Accelerator Facility

In the very first figure in the first paper to appear in Surface and Interface Analysis, Seah and Dench displayed the kinetic energy dependence of the electron IMFP in solids. They and others, especially Cedric Powell, have pursued this issue relentlessly. Their work was seminal, pointing to the opportunity for non-destructive depth profiling by tracking emission from a particular element core level while varying photon energy. The opportunity was a motivation for construction of photoemission beamlines at synchrotron sources. We have used the soft x-ray undulator line (X1B) at National Synchrotron Light Source to study the near-surface structure of niobium. Niobium is the material of construction for superconducting radio-frequency (SRF) cavities at the heart of most new particle accelerators. The International Linear Collider is proposed to comprise some 16,000 Nb SRF cavities. The microwave rf penetrates only a few tens of nm into the Nb surface, lending great importance to optimizing it. Much is determined by the final post-fabrication steps, typically chemical etching or electropolishing followed by low temperature baking. While many characterization techniques can be applied, variable photon energy XPS has the added advantage that it does not alter the material examined. A specimen can therefore be examined at successive treatment stages, followed by SRF performance measurements.

11:20am **AS-MoM11 Formation of Ultra Thin Oxide Free Protective Coatings on Chromium and 316 L Stainless Steel from Etidronic Acid**, *S.L. Johnson,* ***P.M.A. Sherwood***, Oklahoma State University

We have reported many examples of how thin (10nm or less) oxide free films can be formed on a number of metals. In this work we report how the use of etidronic acid (1-hydroxyethylidene-1,1-diphosphonic acid (hydroxy-ethyl diphosphonate or HEDP)) can form such films, providing an example of how an organophosphorus acid can form thin oxide free films in addition to the films previously reported for phosphorus acids. The films formed were produced on the surface of metallic chromium and on 316 L stainless steel by treatment by 3 molar etidronic acid using an anaerobic cell and a"bench" treatment. Core level and valence band X-ray photoelectron spectroscopy (XPS) were used to study the films formed. Compositional variations were interpreted through the use of band structure and X-alpha calculations. Valence band photoemission spectra interpreted in this manner were found to be effective in understanding subtle differences in the resulting surface chemistry as well as in identification of the various phosphates structures. The chromium foil experimental results indicate that the etidronate broke up and formed a phosphide on the surface. The anaerobic cell treatment of the chromium foil produced an extremely thin layer which consists of a phosphate which appears characteristic of chromium orthophosphate indicating that the etidronate molecule did not remain intact. Polished 316L stainless steel treated in 3 M etidronic acid formed a thin film when using the "bench"treatment, but a film characteristic of etidronate when the anaerobic cell was used. This thin etidronate film result shows that oxide-free etidronate films can be formed on stainless steel which may find application in implant fabrication.

11:40am **AS-MoM12 X-ray Photoemission Analysis of Chemically Treated CdZnTe Semiconductor Surfaces**, ***A.J. Nelson***, *A.M. Conway, R.A. Bliss, C Evans, J.L. Ferreira, R.J. Nikolic, S.A. Payne*, Lawrence Livermore National Laboratory

Device-grade $Cd_{(1-x)}Zn_xTe$ was subjected to various chemical treatments commonly used in device fabrication to determine the resulting microscopic surface composition/morphology and the effect on contact formation. Br:MeOH (2% Br), N_2H_4, NH_4F/H_2O_2, and $(NH_4)_2S$ solutions were used to modify the surface chemistry of the $Cd_{(1-x)}Zn_xTe$ crystals. Scanning electron microscopy was used to evaluate the resultant surface morphology. Angle-resolved high-resolution photoemission measurements on the valence band electronic structure and Zn 2p, Cd 3d, Te 3d, O 1s core lines were used to evaluate the chemistry of the chemically treated surfaces. Metal overlayers were then deposited on these chemically treated surfaces and the I-V characteristics were measured. The measurements were correlated to understand the effect of interface chemistry on the electronic structure at these interfaces with the goal of optimizing the metal/$Cd_{(1-x)}Zn_xTe$ Schottky barrier for radiation detector devices.

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Applied Surface Science

Room: 610 - Session AS-MoA

Quantitative Surface Analysis II. Electron Spectroscopies: (Honoring the contributions of Martin Seah, NPL, and Cedric Powell, NIST)

Moderator: S. Asher, National Renewable Energy Laboratory

2:00pm **AS-MoA1 Cluster Primary Ion Beams Advance the Capability of Bio-Molecule Analysis by SIMS**, ***J.C. Vickerman***, The University of Manchester, UK **INVITED**

The analysis of bio-molecular systems using SIMS with atomic primary ion beams has been bedevilled by three principal limitations - the static limit, the inability to sputter large molecules intact and the very low ionisation probability. The static limit, imposed because of the extensive bombardment induced chemical damage generated by high energy atomic primary ions, limits the amount of material accessible for analysis to 1% of the surface layer, greatly limiting detection sensitivity, the pixel size that can be usefully imaged and eliminating the possibility of molecular depth profiling. Atomic primary ions do not appear to be capable of sputtering intact organic molecules molecular weight much above 500 daltons in significant quantities. This places a major limitation on the value of SIMS in bioanalysis. Finally in common with all desorption mass spectrometries, the ionisation probability of the sputtered species is usually well below 10^{-3}, placing a further limitation on detection sensitivity and the useful minimum pixel size in SIMS imaging. It is clear that making progress into lifting some or all of these limitations would have a dramatic effect on the value of SIMS in bio-analysis. Over the last 10 years the possibility that cluster primary ion beams would lift some of these limitations has been increasingly investigated. The capability of liquid metal ion sources to generate cluster ions such as Au_n^+ and Bi_n^+ has been exploited.[1,2] Gas sources have been used to deliver SF_5^+ and C_{60}^+ ions.[3,4] It has been shown that these ions can greatly increase the yield of higher mass ions by orders of magnitude and enable ions up to ~3000 daltons to be detected. Nevertheless the metal cluster ions still generate significant bombardment induced chemical damage such that the static limit is still necessary.[5] However the larger cluster ions such as C_{60}^+ generate far less bombardment induced chemical damage and for many systems the static limit can be lifted.[5] This greatly increases the potential for high sensitivity analysis, imaging with sub-micron resolution and most significant - molecular depth profiling.[6] This latter development offers the possibility of 3D molecular imaging of bio and organic systems.[7] This paper will review the progress that has been made and will suggest that to fully exploit the benefits of cluster primary ions new approaches to analysis may be required.

[1] N. Davis, D.E. Weibel, P. Blenkinsopp, N. Lockyer, R. Hill, J.C. Vickerman, App. Surf. Sci 203-204 (2003) 223-227

[2] F. Kollmer, App. Surf. Sci 231-232 (2004) 153-158

[3] C.M. Mahoney, S.V. Robertson, G. Gillen, Anal. Chem. 76 (2004) 3199-3207

[4] D.E. Weibel, S. Wong, N.P. Lockyer, P. Blenkinsopp, R. Hill, J.C. Vickerman, Anal. Chem. 75 (2003) 1754-1764

[5] E.Jones, N.P. Lockyer and J.C. Vickerman, Int J, Mass Spectrom., 260 (2007) 146-157

[6] J. Cheng, A. Wucher and N. Winograd, J. Phys. Chem. B 110, 8329-8336 (2006).

[7] J. S. Fletcher, N. P. Lockyer, S. Vaidyanathan, and J. C. Vickerman, Anal. Chem., 79 (2007) 2199-2206

2:40pm **AS-MoA3 Detector Dead-time Effects in the Multivariate Analysis of ToF-SIMS Spectral Images**, ***M.R. Keenan***, Sandia National Laboratories, *V.S. Smentkowski*, General Electric Global Research, *J.A. Ohlhausen*, Sandia National Laboratories

The time-to-digital converters typically employed for ToF-SIMS have a dead-time that is significant with respect to the distribution of times-of-flight characteristic of a given nominal mass. When data are acquired with high mass resolution, it is generally the case that only a single secondary ion can be detected at any given mass per primary ion pulse, regardless of how many ions actually reach the detector. Consequently, the data become non-linear in the sense that the signal intensity is no longer proportional to the local composition. This phenomenon often manifests itself as "saturation," for instance, finding isotope ratios that deviate significantly from generally accepted values. The data non-linearity also poses significant problems for multivariate statistical analysis techniques (MVSA), which fundamentally assume an underlying linear additive model. In these cases, extraneous components are often discovered that simply describe the non-linearity and can ultimately confound chemical interpretation. Dead-time correction procedures have been described, previously, for time-of-flight mass spectrometry. These typically rely upon observing a statistically significant number of ion pulses at each volume element, a situation that is not practical for ToF-SIMS spectral images composed of large numbers of pixels, 3D depth profiles and stage rastering measurements. In this paper, various dead-time effects on ToF-SIMS spectral images will be described. We will also propose a novel data pretreatment protocol that is suitable for use with MVSA. The new method involves a transformation to linearize the data, which is similar to previously published corrections, together with a scaling step to properly account for the non-uniform noise characteristic of dead-time-limited data. The ability of the new protocol to enable the extraction of accurate, meaningful components while excluding noise during MVSA will be illustrated with simple, intuitive examples.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

3:00pm **AS-MoA4 Quantitative Nanoscale Analysis of Surfaces with Topography using ToF-SIMS**, *J.L.S. Lee*, ***I.S. Gilmore***, *M.P. Seah*, National Physical Laboratory, UK

Surface topography is a crucial issue for the analysis of innovative devices such as microfluidic systems, MEMS devices, fibres, composite materials, sensors, organic electronics and biomedical devices. The strength and durability of these components is critically dependent on their nanoscale surface chemistry and molecular interactions. However, quantitative characterisation of surfaces with topography remains a significant challenge due to the lack of systematic and validated measurement methods.[1] In particular, surface topography can causes many unwanted artefacts in ToF-SIMS spectra and images, including ion shadowing effects caused by distortions in the extraction field, reduced mass resolution caused by the spread in the time of flight of secondary ions, distortions in the images due to the angular differences between the primary ion beam and the analyser with respect to the sample, loss in signal due to the limited angular acceptance of the analyser, and potential problems in charge compensation of insulating samples. This presents enormous technical challenges to process engineers and R&D scientists developing new products and processes. Here, we present a systematic study of the effects of surface topography on SIMS. Experimental data are acquired for model cylinders, fibres and spheres, for both conducting and insulating samples. The results are in good agreement with those obtained using an ion optics simulation program, SIMION,[2] allowing us to understand the effects of surface topography and provide guidance to practical analysts for identifying and reducing topographical effects. In addition, the use of multivariate methods for images with surface topography is investigated using principal component analysis (PCA) and multivariate curve resolution (MCR), extending from our previous work on mixed organic systems on flat surfaces.[3] With careful application and suitable data preprocessing methods, multivariate analysis is shown to improve data interpretation and allows for the rapid processing of high-resolution raw spectral data in SIMS images.

[1] S Rangarajan and B J Tyler, J. Vac. Sci. Technol. A 24(5) (2006) 1730-1736

[2] SIMION version 8.0, Scientific Instrument Services, Inc., 1027 Old York Rd., Ringoes, NJ 08551, USA

[3] J L S Lee, I S Gilmore and M P Seah, submitted.

3:40pm **AS-MoA6 Cluster Primary Ions: Spikes, Sputtering Yields, Secondary Ion Yields and Inter-Relationships for Secondary Molecular Ions for Static SIMS**, ***M.P. Seah***, National Physical Laboratory, UK **INVITED**

A framework is provided to describe the enhanced sputtering yields and secondary ion yields of molecular fragments, from molecules on substrates, achieved when using cluster primary ions. Analysis of published sputtering yield data shows that one particular model of sputtering, that includes spikes, is an excellent quantitative description of the yields for a wide range of monatomic and polyatomic primary ions. Evidence will be shown of the model validity for clusters of up to more than 10 atoms over 3 orders of magnitude in sputtering yield. Using data from one primary ion, within this model, extremely good descriptions of measurements reported with other primary ions is achieved. This theory is then used to evaluate the important molecular ion yield behaviour for static SIMS. This leads to universal dependencies for the de-protonated molecular ion yields, valid for all primary ions, both single atom and cluster, over 5 decades of emission intensity. This formulation permits the prediction of the $(M-H)^-$ secondary ion yield for different, or new, primary ion sources, e.g. Bi_n^+ and C_{60}^+, for the analysis of organic materials. Optimal primary ion sources are predicted and discussed. For analysing materials, raising the molecular secondary ion yield is extremely helpful but it is the ratio of this yield to the disappearance cross section that is critical. Data are evaluated and a description is given to show how this varies with the cluster type to provide a further universal dependence. Optimal analytical conditions are discussed.

4:20pm **AS-MoA8 The 3D Atom Probe Instrument - Introduction to the Technique and Some Applications in Material Science**, ***L. Renaud***, CAMECA, France **INVITED**

The 3D atom probe is a quantitative technique that provides atomic scale 3D element mapping of chemical heterogeneities in sample.[1] The sample has to be prepared in the form of a very sharp tip. Under the effect of high electrical field, the atoms at the surface are evaporated by field effect and projected on a position sensitive detector.[2] This detector allows the localization of the impacts in synchronism with the measurement of the time of flight of the evaporated atoms. At the end of the analysis, it is possible to rebuild in 3D near an atomic scale, the analyzed volume (typically 70nm x 70nm x 200nm), atom by atom. The goal of this presentation is to demonstrate the contribution of the 3D-AP in materials science. For this purpose, we will make first a brief introduction to the technique. Some results obtained with this technique will be shown in order to evaluate the contribution of the instrument in materials science (especially for quantification measurement). In the last part of the presentation, new developments and future applications of the instrument will be discussed and also we will make an insight to the sample preparation issue

[1] D. Blavette et al., Nature 363 (1993) 432 - 434

[2] L. Renaud et al., Nuclear Instruments and Methods in Physics Research Section A: Vo 477, Issues 1-3, 21 January 2002, 150-154

5:00pm **AS-MoA10 Composition of Surfaces: A Comparison of LEIS and ToF-SIMS**, *D. Breitenstein, R. Kersting,* ***B. Hagenhoff***, Tascon GmbH, Germany, *R. ter Veen, H. Brongersma*, Calipso B.V., The Netherlands

Low Energy Ion Scattering (LEIS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) enable the analysis of the atomic and chemical surface composition of vacuum sustainable samples. Applying LEIS, the surface of a sample is hit by noble gas ions (He^+, Ne^+, ...) of low energy (1-5 keV). Elastic collisions with individual surface atoms can cause backscattering of the projectiles. Analyzing the energy of these scattered noble gas ions, and moreover knowing their mass and initial energy, the identity of the atomic collision partner can be calculated. Therefore, LEIS enables the quantitative determination of the elemental composition of the samples‘ outermost monolayer. Ions scattered in deeper layers, loose extra energy along the in- and outgoing trajectories. This is used to obtain non-destructive high-resolution depth profiles (0-10 nm). In ToF-SIMS the surface of the samples is also bombarded with atomic - or even polyatomic - projectiles. In contrast to LEIS the energy (10-25 keV) and the mass (e.g. Bi_3^+: 627 u) of these projectiles is relatively high. The impact of these projectiles leads to a formation of collision cascades in surface near regions resulting in a desorption of particles (electrons, neutral and ionized atoms as well as molecules). The ions can be mass separated and detected in a ToF analyzer providing elemental and molecular information on the first 1-3 surface monolayers. Both techniques provide useful information on the surface composition of solids. However, this information differs for LEIS and ToF-SIMS in several aspects: Firstly, LEIS offers the lower information depth. Whereas ToF-SIMS probes the uppermost three monolayers, LEIS generates information on the outermost monolayer. Secondly, ToF-SIMS offers information on the elemental as well as molecular composition of the surface, whereas with LEIS solely elemental information can be obtained. Furthermore, in terms of quantification, LEIS is superior to ToF-SIMS. Finally, ToF-SIMS allows a laterally resolved probing of the sample down to a resolution of 100 nm whereas in LEIS the lateral resolution is restricted to 0.1-1 mm. This paper compares results of applying LEIS as well as ToF-SIMS to well-defined samples such as Langmuir-Blodgett monolayers but also to analytically relevant samples like nanoparticles. It will highlight the strengths of both techniques and the synergism obtained in applying both methods.

Applied Surface Science

Room: 610 - Session AS+BI+NS-TuM

Surface Analysis and Related Methods for Biological Materials

Moderator: J. Soares, University of Illinois at Urbana-Champaign

8:00am **AS+BI+NS-TuM1 Nano-bio Chemical Image of Single Cells and Tissues for Bio-medical Applications**, ***D.W. Moon***, *T.G. Lee, J.Y. Lee*, Korea Research Institute of Standards and Science **INVITED**

Biochemical imaging of cells and tissues is a basic infra-technology in various bio-medical applications. Instead of conventional labeling methodology for biomolecular imaging with fluorescent dyes, label-free single cell and tissue biochemical imaging methodologies such as a nonlinear optical technique, coherent anti-Stokes Raman scattering (CARS) and an ion beam sputtering analysis technique, Secondary Ion Mass Spectrometry (SIMS) using cluster ion beams were developed. They were used to measure in a complementary manner 2D or 3D biochemical images of various cells and tissues such as Hella cells, adipogenic stem cells, fat liver tissues, cancer tissues, and skin tissues. Preliminary results will be discussed on the following issues. 1) Interactions of fibroblasts with native and denatured collagen thin films were studied with CARS and SIMS. It was extended to study the interactions of fibroblasts with 500 nm nano-fibers and 5 µm micro-fiber made of 40% poly (glycolic acid) (PGA) and 60% collagen. 2) Photoaging effects of skin by UV radiation were studied with SIMS, which showed significant changes in the biochemical imaging of amino acids representing collagen fibers and lipid molecules. 3) It was shown that SIMS imaging of colon cancer tissues has some potential to develop personalized cancer therapy with new drugs. Finally, the present status and future prospects of nano-bio technology based on laser, mass spectrometry, and nanoprobe for biochemical imaging of single cells and tissues at KRISS will be discussed for practical applications in bio, medical, and pharmaceutical researches.

8:40am **AS+BI+NS-TuM3 SIMS Imaging of Polymer Membranes and Single Cells**, ***G. Jiang***, *R. Michel, D.J. Responte, L. Mayorga, K. Greenland, T.N. Davis, T.A. Horbett, D.G. Castner*, University of Washington

The ability to obtain 3-D images of drug distributions in polymers can provide information about drug loading and release profiles. Likewise 3-D images of biological species (lipids, proteins, sugars, etc.) in cells can provide information about the distribution of those species within the cell. With the advent of C_{60} cluster ion beam sources, it is now possible to use time-of-flight secondary ion mass spectrometry (ToF-SIMS) to examine these important biological problems. This study used a dual beam approach (C_{60}^+ for sputtering and Bi_1^+ or Bi_3^+ for analysis) to generate 3-D images from drug (dipyridamole) loaded polyurethane (PEU) films cast onto glass and single cells (yeast and monocytes) adsorbed onto porous polycarbonate (PC) membranes. 3-D images were successfully obtained from all samples. For PEU films without the drug, the intensity of organic fragment ions from the PEU remained constant until the PEU/glass interface was reached, then decreased as the intensity of fragments from the glass increased. In the initial stages of sputter profiling drug loaded PEU films, the intensity of the drug peaks decreased while the intensity of the PEU fragments increased. Then intensities from both components remained relatively constant until the PEU/glass interface was reached. Molecular ions from the drug were readily detected throughout the entire PEU film. ToF-SIMS 2-D and 3-D images of single yeast (size ~ 5 microns) and monocyte (size ~ 10 microns) cells were obtained for cells adsorbed onto the surface of the PC membrane and within the pores of the PC membrane. Fragments from biological species from these cells (e.g., phospholipid at m/z = 184) could be detected in the ToF-SIMS images. These results indicate the possibility of 3-D chemical state mapping of single cells and other biomedical samples with the spatial resolution of a few microns.

9:00am **AS+BI+NS-TuM4 Surface Energy Control Within Copolymer Libraries Synthesised as Micro Arrays for Biological Screening**, *M. Taylor, A.J. Urquhart,* The University of Nottingham, UK*, D.G. Anderson, R. Langer,* Massachusetts Institute of Technology*, M.C. Davies,* ***M.R. Alexander***, The University of Nottingham, UK

There is currently much interest in polymer microarrays in the field of high-throughput materials development.[1,2] Although combinatorial material synthesis is relatively advanced, methods for characterising the surface chemical properties of such libraries are less well developed. We report on methods to characterise the surface chemistry and surface energy of 480 polymers on a microarray formed using on-slide copolymer synthesis. We used X-ray Photoelectron Spectrometry and Time of Flight Secondary Ion Mass Spectrometry to provide surface chemical information from each spot. Water and diiodomethane contact angle measurements were made from individually dosed picolitre volume droplets to estimate surface energy of each copolymer formulation.[3] Such arrays provide extra challenges for characterisation due to the large sample numbers, small sample size and increased data volume. Here, we will focus on the correlations determined between the monomer structures and the surface energy. The information XPS and SIMS can provide on the actual surface chemistry is presented and contrasted to the bulk surface chemistry. We highlight the ability to tune the surface energy using certain polymerised monomer combinations by varying their relative concentrations. This has great utility in controlling the biological response to polymer surfaces.

[1] J. A. Hubbell, Nature Biotechnology 2004, 22, 828.

[2] D. G. Anderson, S. Levenberg, R. Langer, Nature Biotechnology 2004, 22, 863.

[3] Taylor, M.; Urquhart, A. J.; Zelzer, M.; Davies, M. C.; Alexander, M. R., Picolitre water contact angle measurement on polymers. Langmuir Letters (2007, in press).

9:20am **AS+BI+NS-TuM5 Surface Characteristics of Listeria Monocytogenes Mutants with Variable Pathogenicity Levels**, ***N.I. Abu-Lail***, *B.-J. Park*, Washington State University

Despite being an important food-borne pathogen, L. monocytogenes in fact comprises a diversity of strains with varying virulence. Whilst many strains of L. monocytogenes have pathogenic potential and can result in disease and mortality, others have limited capability of establishing infections and relatively avirulent. Although very important, the question of how the composition of the bacterial surface and the properties of bacteria vary between strains that have different level of virulence at the molecular level needs to be answered. To answer this question, interaction forces between five different L. monocytogenes mutants that vary in their virulence and a model surface of silicon nitride were investigated using atomic force microscopy (AFM). Adhesion measurements between the strongest Listeria mutant and silicon nitride reveled that although both surface polysaccharides and surface proteins contributed significantly to the total adhesion, polysaccharides contribution (1.0 ± 0.2 nN) was larger than that of proteins' contribution(0.38 ± 0.1 nN). Adhesion forces were also dependent on the pH value of the solution, temperature, and media type. Experiments on intermediate virulence mutants and avirulent mutants are currently ongoing. Successful completion of these experiments will improve our understanding of the main molecular differences between virulent and avirulent strains of L. monocytogenes. Such findings would be very important, because it will allow for the first time and at a molecular level, to define a criteria that can distinguish virulent L. monocytogenes' strains from avirulent ones and therefore reduce unnecessary recalls of food products and help in preventing disease outbreaks.

9:40am **AS+BI+NS-TuM6 First Observation of Charge reduction and Desorption Kinetics of Multiply Protonated Peptides Soft Landed onto Self-assembled Monolayer Surfaces**, ***O. Hadjar***, *J.H. Futrell, J. Laskin*, Pacific Northwest National Laboratory

Soft-landing (SL) of hyperthermal ions onto semiconductive surfaces is a promising approach for highly-selective preparation of novel substrates using a beam of mass-selected ions. In addition, controlled deposition of complex ions onto surfaces presents a new approach for obtaining molecular level understanding of interactions of large molecules and ions with a variety of substrates relevant for biology and catalysis research. In this work we present a first study of the kinetics of charge reduction and desorption of peptide ions soft-landed onto a fluorinated self-assembled monolayer (FSAM) surface at hyperthermal energy (40 eV). An in situ 8 keV Cs^+ secondary ion mass spectrometry (SIMS) in a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer is used. Doubly protonated peptide ions are produced by electrospray ionization, mass-selected and transferred to the surface. The experiment allows the Cs^+ beam to merge with the peptide ion beam on the surface facilitating real time soft landing process monitoring. The surface is regularly probed using SIMS during and after ion soft-landing. All peptide-related peaks in SIMS spectra show a gradual increase during the soft-landing. Rapid decay of the $[M+2H]^{2+}$ signal accompanied by increase of the $[M+H]^{+}$ signal is observed after soft-landing is stopped. The $[M+H]^{+}$ signal maximizes 2-3 hours after the end of the soft-landing and shows a relatively slow time decay at longer delay times. Several peptide fragments followed a very different kinetics behavior showing very slow, almost linear decay after soft-landing. We attribute this time signature to fragments that originate from neutral peptide molecules on the surface. Other peptide fragments show a mixed behavior suggesting that they are formed from different charge states of the soft-landed peptide ions. Our results demonstrate for the first time that various peptide-related peaks follow very different kinetics, signatures for doubly protonated, singly protonated and neutral peptides retained on the surface. The experimental results are in excellent agreement with a simple kinetic model that takes into account charge reduction and desorption of different species from the surface. The kinetic modeling allowed us to obtain for the first time desorption and charge exchange rate constants for different peptide species on the surface.

10:40am **AS+BI+NS-TuM9 Ultra Fast Mid Infrared Spectroscopic Imaging for Biomedical Applications**, ***J. Phillips***, *H. Amrania, J. Plumridge, M. Frogley*, Imperial College London, UK

We discuss the potential biomedical applications for a unique infrared spectroscopic micro-imaging system. A table top tuneable solid state laser has been coupled to a commercial infrared microscope to create a unique mid-IR imaging tool. By integrating with a modified high resolution infrared camera that has previously only been available to the military market, we have constructed a broadband imaging system capable of performing diffraction limited spatially resolved spectroscopy of biological specimens. The narrow line-width of the laser allows us to take spectra at a resolution of 20cm-1. A polymer film sample with a micron scale structure has also been imaged in reflective mode to resolve details down to 8 microns in size. We also discuss results from spectrally imaging cancerous cervical tissue samples. The high peak power of the laser (10MW) offers signal to noise levels previously unobtainable with stand-alone laboratory based commercial instruments. This coupled with a short pulse duration will for the first time enable time resolved imaging at a 100psec resolution.

11:00am **AS+BI+NS-TuM10 X-ray Spectromicroscopy and Ion Spectroscopy to Evaluate a Blend of Poly(L)lactic Acid and Fluorine End-capped Poly(L)lactic Acid**, ***D. Wells***, *J.A. Gardella*, University at Buffalo

Blending polymers is a versatile method for tuning the physical and chemical characteristics of a material such as strength, thermal stability, optical properties, and degradation rates. As the field of nanomaterials continues to grow it is essential to be able to evaluate the microstructure of polymeric materials as well as to characterize the chemistry that occurs at the interfaces of blended polymer films. Two techniques capable of such analysis are scanning transmission X-ray microscopy (STXM) and imaging time of flight secondary ion mass spectrometry (ToF-SIMS). STXM is a spectromicroscopy technique, that is, it combines both imaging and chemical spectral information. Recent advancements in cluster primary ion sources for ToF-SIMS have extended the range of its applications. The system of primary interest in this work is a blend of poly(L)lactic acid (PLLA) with fluorine end-capped poly(L)lactic acid (F-PLLA). This material has potential as a drug delivery device whose degradation could be controlled by changing the ratio of hydrophobic F-PLLA to hydrophilic PLLA. It is known that the fluorine containing component will preferentially surface segregate.[1] By reducing the concentration of F-PLLA we predict that we can create lateral surface segregation as well as vertical segregation. Both STXM and ToF-SIMS generate images containing chemical information and are useful to evaluate lateral phase segregation. Our intent is to use these two techniques as the primary means to evaluate the effects of changing the ratio of F-PLLA to that of pure PLLA.

[1] Won-Ki Lee, I. L., Joseph A. Gardella Jr., Synthesis and Surface Properties of Fluorocarbon End-Capped Biodegradable Polyesters. Macromolecules 2001, 34, (9), 3000-3006.

11:20am **AS+BI+NS-TuM11 Influence of Molecular Environment on ToF-SIMS Detection of Bio-Active Molecules on Self-Assembled Monolayers**, ***Z. Zhu***, Pacific Northwest National Laboratory

Bio-active molecules can be immobilized on solid substrates to form a monolayer or sub-monolayer. Because interactions between bio-active molecules are typically special, this structure is very useful in bio-recognition. So far, it has been widely used in bio-analysis or disease diagnosis. Alkanethiol self-assembled monolayer (SAM) on Au substrate is one type of commonly used solid substrate due to its versatile surface properties. During the last decade, time-of-flight secondary ion mass spectrometry (ToF-SIMS) has proven one of the most convenient techniques to detect sub-monolayer of organic molecules on alkanethiol SAMs. We have earlier described the possibility of quantitative detection of peptide molecules on COOH-terminated SAMs. However, we found that molecular environment greatly affect the signal intensity. For example, Au+ signal from -S(CH2)2(CF2)9CF3 film is much stronger than Au+ signal from S(CH2)11CO2H film. Therefore, quantitative comparison of the density of bio-active molecules on different SAMs by ToF-SIMS is difficult unless effect of molecular environment can be quantitatively considered. In this work, a number of bio-active molecules were deposited on -S(CH2)11CH3, -S(CH2)10OH, -S(CH2)10CO2H, and -S(CH2)2(CF2)9CF3 films with similar density, and ToF-SIMS measurements were made. Two major factors are found to affect SIMS signal intensity. Firstly, electron-attraction organic functional groups are found to enhance positive ion signals but depress negative ion signals. For example, positive ion signals are enhanced on -S(CH2)2(CF2)9CF3 film but negative ion signals are depressed. In addition, active H-atoms such as those from COOH groups are able to enhance signal of positive molecular ions since they are normally protonated.

11:40am **AS+BI+NS-TuM12 Advances in Organic Depth Profiling Using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) under Optimized Ion Beam Conditions**, *H.-G. Cramer, T. Grehl*, ION-TOF GmbH, Germany, *N. Havercroft*, ION-TOF USA Inc., *F. Kollmer, R. Moellers*, ***E. Niehuis***, *D. Rading*, ION-TOF GmbH, Germany

Depth profiling of inorganic materials has been one of the most important applications of SIMS in general, and more recently also of TOF-SIMS. In contrast, depth profiling of organic materials has always suffered from the fact that high-mass molecular information, to a large extent, is rapidly lost under high-dose sputtering conditions. With the advent of cluster ion beams, however, more and more examples of successful organic depth profiling have been presented, such as C_{60} profiling of PMMA, PLA, etc. On the other hand, it also became obvious that the projectiles and conditions commonly used were not successful for profiling of every organic material analyzed. In this paper we used the so-called dual beam mode of depth profiling to start a systematic investigation of organic depth profiling with a TOF-SIMS instrument. Similar to the case of inorganic profiling, we found the dual beam mode beneficial because sample erosion and the sample analysis are decoupled and can be independently optimized. We applied different primary projectiles, such as C_{60}, Bi_n cluster ions, O_2 and Cs with a wide range of impact energies to a variety of organic specimens. The results will be discussed with respect to the specificity of the detected ions, their yields, the damaged and removed sample volume per primary ion, and classical figures of merit such as depth resolution.

12:00pm **AS+BI+NS-TuM13 Fragment Free Mass Spectrometry for Bio-Molecular Surfaces with Size Selected Cluster SIMS**, ***J. Matsuo***, *S. Ninomiya, K. Ichiki, Y. Nakata, T. Aoki, T. Seki*, Kyoto University, Japan

Polyatomic and cluster ions have been utilized for bio-molecular analysis as the primary ion beam for SIMS. Enhancement of sputtering and secondary ion yields, and the capability for depth profiling of bio-materials have been reported for cluster ions, and are due to the effects of multiple collisions and high-density energy deposition of such ions on solid surfaces. In bio-molecular analysis, not only molecular ions, but also fragment ('daughter') ions are usually observed in the mass spectra, and this makes interpretation of the spectrum difficult. Therefore, reducing fragment ions is very important especially for practical applications. These phenomena strongly depend on cluster size, which is a unique parameter, and one of the fundamental questions is what size of cluster ion is most appropriate for bio-SIMS. To date there have been very few studies on the effect of size on secondary ion emission from bio-molecules. We have examined the size dependence of the secondary ion emission from amino acid, sugar and small peptide films with large cluster ion (N>100) by using the double deflection technique. When the total energy of the cluster ion is fixed, the secondary ion emission (SI) yield of molecular ions increases with size due to the non-linear effect. However, when the cluster size is too large, the SI yield is gradually diminished, because the energy per atom becomes too low to emit secondary ions. The maximum molecular SI yield from amino acid film was obtained for Ar clusters with the size of a few hundred at the energy of 20keV. The ratio of fragment ions to molecular ions was also measured as a function of cluster size. The ratio decreases quite rapidly with increasing the cluster size. When the cluster size was larger than 1000, very few fragment ions were observed in the mass spectrum. In this case, each incident Ar atom has kinetic energy of a few eV, which is comparable to the bonding energy of peptides. Ultra-low energy SIMS can be realized by using large cluster ions. The size effect in secondary ion emission and damage cross-section will be discussed.

Applied Surface Science

Room: 610 - Session AS-TuA

3-Dimensional Characterization

Moderator: S.J. Pachuta, 3M Company

1:40pm **AS-TuA1 XPS, TEM, and SIMS Analysis of FIB Bombarded Surfaces Over the Range 500 eV to 30 keV**, ***J.E. Fulghum***, *K. Artyushkova*, University of New Mexico, *L.A. Giannuzzi, B. Van Leer, J. Ringnalda*, FEI Company, *F.A. Stevie, D.P. Griffis*, North Carolina State University

Focused Ion Beam (FIB) instruments are known for the ability to provide material removal with a lateral resolution less than 10nm using a Ga+ beam. FIB capabilities continue to improve with low energy performance that allows routine use of glancing angle 2kV Ga+ beams for final polishing of TEM specimens. The lower energy reduces the penetration of gallium into the material under study and minimizes sample damage.[1] It is now routinely possible to reduce the energy of the Ga+ beam to 500eV. Previous work has shown that low energy Ga+ impinging at normal incidence results in Ga deposition.[2] There is also TEM evidence indicating that the use of Ga+ for glancing incidence polishing at energies below 2 keV does not further reduce surface damage in Si, but rather creates a Ga rich region since the sputter yield at these energies drops to a value less than 1.[3] An FIB was used to sputter craters into (100) Si using normal incidence Ga energies from 500eV to 30keV. XPS and SIMS analyses were performed on these craters to determine the Ga surface concentrations and depth distributions at these energies. From 30keV down to 2keV, a decreasing Ga penetration was noted. For the SIMS analyses below 2keV, a surface effect was observed in the SIMS depth profiles which may be the result of an enhancement of silicon secondary ion yield. It my be that glancing incidence polishing at Ga+ energies below 2keV will not result in additional reduction of surface damage. However, the low energy FIB capabilities can provide a means for site specific deposition of Ga when the low energy Ga impinges at normal incidence.

[1] L. Giannuzzi, R. Geurts, J, Ringnalda, Microscopy and Microanalysis Proceedings 11 (Suppl 2) 2005, p.828

[2] D.H. Narum and R.F.W. Pease, J. Vac. Sci. Technol. B6(6) (1988) p. 2115

[3] L. A. Giannuzzi, B. Van Leer, J. Ringnalda, Microscopy and Microanalysis Proceedings (2007).

2:00pm **AS-TuA2 3-D XPS Characterization of Organics Surfaces**, ***J.S. Hammond***, *S. Raman, J. Moulder*, Physical Electronics, *N. Sanada, R. Inoue, M. Suzuki*, ULVAC-PHI

For many industrial products, non-uniform surface segregation and contamination of organic constituents on micro-areas of polymeric materials is of great concern. Over the past three years, C60 ion beams have been shown to be very effective for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage. By combining a C60 ion gun system with a scanning x-ray microprobe XPS specifically designed for optimum performance for micro-area spectroscopy, chemical state mapping and depth profiling, it is now possible to obtain a three dimensional characterization of organic surfaces. To illustrate this new analytical technique, surface area mapping and micro-area depth profiling of a coated human hair and a micro-area contamination analysis on a thick polymer will be discussed. By using high energy resolution core level spectroscopy as well as valence band chemical state mapping, information on the coating thickness and the spatial dimensions of contamination areas can be obtained. Finally, a comparison between the chemical state damage induced by the C60 ion beam versus the x-ray beam damage during a depth profile will be discussed. Initial experiments indicate that for some polymers, the x-ray beam damage is of greater significance than the chemical changes observed after C60 sputtering. The use of a scanning x-ray beam may facilitate chemical state depth profiling with minimal data artifacts.

2:20pm **AS-TuA3 C60 Molecular Depth Profiling: A Fundamental Study using a 3D Organic System**, ***A.G. Shard***, *I.S. Gilmore*, National Physical Laboratory, UK

C_{60} sputtering of organic materials enables the possibility of producing 3 dimensional reconstructions of the distribution of organic compounds. We demonstrate that many organic materials have identical yield volumes (volume sputtered per incident ion) and that, in general, sputtering yield is a well behaved function of ion dose. Irganox layers were created by vacuum evaporation to create well-defined stacks of organic materials with controllable layer thicknesses. These layered materials were employed to determine the energy dependence of sputtering yield, depth resolution and damage accumulation during C_{60} depth profiling. We show that sputtering yield increases with C_{60} ion energy and that depth resolution concomitantly becomes poorer. The multilayers are also used to demonstrate how the depth resolution degrades with depth and a comparison with AFM data shows that the resolution is mainly limited by topography. Examples are also shown of the lateral and depth distribution of mixed organic systems.

2:40pm **AS-TuA4 Prospects for Electron Tomography with Atomic Resolution**, ***C.F. Kisielowski***, Lawrence Berkeley National Laboratory, *F.R. Chen*, National Tsing Hua University, Taiwan **INVITED**

Since several decades Transmission Electron Microscopy (TEM) is a primary tool for characterizing the inner structure of materials including interfaces and surfaces. A most limiting factor of the transmission-imaging mode comes with the projection of the probed crystal volume into one image plane, which causes loss of information about the materials structure along the electron beam direction. In recent years electron tomography was developed and successfully applied to soft and hard materials yielding the three dimensional materials structure with a resolution that can approach 1-2 nm.[1,2] However, it is still impossible to achieve truly atomic resolution because radiation damage can limit the electron dose and because quantitative procedures need yet to be established that would allow recovering the materials structure at atomic resolution reliably from the recorded images. In order to achieve this goal it is essential to solve the phase problem and to remove effects that relate to the dynamic scattering of electrons in a solid. In this talk we describe current efforts that aim at reaching this goal. Our investigations build on recent hardware and software developments that relate to the DoE's TEAM Project,[3] which will provide a next generation of electron microscopes operating between 80 and 300 kV and providing deep sub Ångstrom resolution. We show that the phase problem is reliably solved and that dynamic scattering can be indeed inverted. As a result a full quantification of the samples mean inner potentials becomes possible, which can be used to determine the number of atoms in each imaged atom column together with its chemical composition. If such experiments are executed along a few zone axes it is possible to reconstruct the atomic structure of materials with atomic resolution.[4] Experimental validations of the developed concept include gold surfaces and bi-crystals of Al:Cu.

[1] C.-E. Hsieh, AR Leith a, C. A. Mannella, J. Frank, M. Marko, Journal of Structural Biology 153 (2006) 1-13

[2] Q. Yang, J. Mardinly, C. Kübel, C. Nelson, C. Kisielowski, International Journal of Materials Research 97, (2006) 880-4

[3] http://www.lbl.gov/LBL-Programs/TEAM/index.html

[4] J.R. Jinschek, H.A. Calderon, K.J. Batenburg, V. Radmilovic, C. Kisielowski, Mat. Res. Soc. Symp. Proc. 839 (2005) 4.5.1 - 4.5.6.

4:00pm **AS-TuA8 Retrospective and Multivariate Statistical Analysis of Three-Spatial-Dimension ToF-SIMS Data Sets**, ***V.S. Smentkowski***, *S.G. Ostrowski*, General Electric Global Research, *M.R. Keenan, J.A. Ohlhausen, P.G. Kotula*, Sandia National Laboratories

3 spatial dimension (3D) Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis can be performed if an X-Y image is saved at each depth of a depth profile. We will show how images reconstructed from specified depths, depth profiles generated from specific X-Y coordinates, as well as 3 spatial dimensional rendering provides for a better understanding of the sample than traditional depth profiling where only a single spectrum is collected at each depth. We will also demonstrate that multivariate statistical analysis (MVSA) tools can be used to perform a rapid, unbiased, analysis of the entire 3D data set. Color overlays of the MVSA components and animated movies showing the visualization (in 3D) from various angles will be provided. The MVSA results will also be represented as depth profile traces. 3D ToF-SIMS analysis is performed using only 1 primary ion shot/pixel. Under these conditions, detector dead time effects can introduce non-linearities into the data sets; examples of non-linear data sets will be shown. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:20pm **AS-TuA9 3D Molecular Characterization of a Drug Delivery System**, ***G.L. Fisher***, Physical Electronics, *A. Belu*, Medtronic Inc., *K. Wormuth*, SurModics Inc.

Coronary implants that incorporate a drug delivery system are being developed at an increasing rate. It is important for a variety of reasons to characterize such in vivo drug delivery devices and to relate the chemical and physical properties to how the system will function. This study focuses on the characterization of a drug eluting stent coating that consists of rapamycin in a poly(lactic-co-glycolic acid) (PLGA) matrix. The goal is to understand the lateral and depth distribution of the drug in the polymer matrix. Additionally, the drug distribution is studied as a function of elution time. Information regarding the lateral and depth distribution of rapamycin in PLGA, and the distribution as a function of elution time, was determined by TOF-SIMS depth profiling with a C_{60} cluster ion source. Where appropriate, the TOF-SIMS results will be compared to the results obtained by XPS and confocal Raman. The experimentally-determined 3D chemical structure as a function of elution time, in conjunction with the elution profiles, may be used to enhance the design of future in vivo drug delivery systems.

4:40pm **AS-TuA10 3D Image Acquiring and Spectrum Extraction from 2D Elemental Mapping in Auger Electron Spectroscopy**, ***N. Urushihara**, S. Iida, N. Sanada,* ULVAC-PHI, Inc., Japan, *D.F. Paul, S. Bryan,* Physical Electronics, *M. Suzuki,* ULVAC-PHI, Inc., Japan, *Y. Nakajima, T. Hanajiri*, Toyo University, Japan

Auger electron spectroscopy (AES) is widely used for observation of two-dimensional map (surface elemental distribution) with a high spatial resolution as well as in-depth elemental distribution. An elemental map is generally obtained at an as-received surface or a sputtered surface. Though it is easy to visually recognize elemental distribution in a plane surface, it is difficult to display it three-dimensionally. On the other hand, an energy dispersal spectrum is not stored at each pixel of an elemental map in AES, and it leads a difficulty to investigate spectral shapes at specified points in an elemental map. In order to solve the former issue we have tried to acquire a three-dimensional elemental map and for the latter issue we have studied to extract an energy dispersal spectrum from successive two-dimensional images at fixed kinetic energies. Specimens used were two kinds of SOI (Silicon on insulator) in the study of 3D image acquiring and a part of sputtered crater at the interface region of a silicon dioxide layer on silicon substrate in the study of spectrum extraction from 2D elemental maps. The interface regions were ion-sputtered at the interval of 0.5nm and intensity distributions of Si LVV and O KLL were mapped at a respective depth with 256 x 256 pixels. One can easily recognize three-dimensional features at the interface regions, seeing successive display of 2D maps. It is clearly seen that silicon oxide is formed island structure for the interface in one of the specimens. For the second issue, two-dimensional signal intensities were stored at the region located adjacent to the interface of SiO_2 and Si on a graded sputtered surface. Maps consisted of 64 x 64 pixels and imaged signal intensities were defined as raw intensities including background components. The maps were obtained in the energy ranges of 77 eV to 100 eV for Si LVV with an energy step of 3 eV. At every pixel point energy dispersal spectra were extracted from the 9 maps obtained at the fixed energy. It is obviously distinguished for extracted Si LVV spectra for silicon elemental component and oxide component. All of extracted spectra were processed with linear least square (LLS) method, resulting in separation of elemental and oxide components. In the presentation, results from other material systems for both issues will be demonstrated.

5:00pm **AS-TuA11 Nanospectroscopy of Single Silicon Nanowire Surface using Energy Filtered X-ray PhotoElectron Emission Microscopy (XPEEM)**, ***O. Renault**, A. Bailly,* CEA-LETI Minatec, France, *N. Barrett, L.-F. Zagonel,* DSM/DRECAM/SPCSI, France, *N. Pauc, P. Gentile,* CEA DRFMC, SiNAPS, France, ***T. Baron***, CNRS-LTM, France

Interest in silicon nanowires (Si NWs) continues to grow, fuelled by novel applications in nanotechnology. This requires precise wire engineering in order to tailor specific surface properties of Si NWs like electron emission properties and surface chemistry, which can be altered by the growth process.[1] Within this perspective, the implementation of novel, non destructive experimental techniques offering both spectroscopic and microscopic capabilities is needed. In this contribution, we present recent results of a surface study using synchrotron radiation induced X-ray PhotoElectron Emission Microscopy (XPEEM) of 250 nm-diameter single NWs dispersed on gold after growth by the Vapour-Liquid-Solid process from gold-silicon catalysts. Here, XPEEM is implemented with the first commercially available NanoESCA spectromicroscope featuring a fully electrostatic PEEM column together with an aberration-corrected energy filter (double hemispherical energy analyser) allowing both a high lateral and energy resolutions.[2-4] The instrument allows laboratory XPEEM experiments with a bright AlKα source, and can also be periodically moved to the European Synchrotron Radiation Facility (ESRF) to benefit from the high brightness and energy tunability of ID08, a soft X-ray beamline.[4] We focus on results related to the energy-filtered, secondary electron images at the photoemission threshold that reveal differences in the local work function and enable investigation, along the nanowire, of the sidewall wetting by the catalyst and the catalyst properties. The double-photoemission threshold shape of the generated nanospectra along the NW surface is a superposition of that characteristic of the Si NW surface and of the gold substrate indicating that gold diffusion and dewetting along the NW sidewall occurs, giving rise to the formation of a non-continuous gold layer. This is confirmed by the Au4f core-level images and SEM observations on the same nanowire. This experiment demonstrates the powerful capabilities of XPEEM nanospectroscopy with the NanoESCA for the surface chemical characterization of single nanostructures.

[1] J.B. Hannon et al., Nature 440 (2006) 69.

[2] M. Escher et al., J. Phys.: Condens. Matter 17 (2005) S1329.

[3] O. Renault et al., Surf. Interface Anal. 2006 ; 38 : 375-377.

[4] O. Renault et al., Surf. Sci. 2007 (in press).

Applied Surface Science

Room: 4C - Session AS-TuP

Aspects of Applied Surface Science Poster Session

AS-TuP1 Exploring the Complementary Nature of ToF-SIMS and ESCA Depth Profiling, ***K.G. Lloyd***, *L. Zhang, J.R. Marsh, M.A. Plummer*, The DuPont Company

Depth profiling -- the removal of material with nanometer depth resolution while analyzing with surface-specific techniques that probe only the newly-revealed surfaces – is an important characterization component of the electronics industry. Secondary Ion Mass Spectrometry (SIMS) and X-ray Photoelectron Spectroscopy (XPS, a.k.a. ESCA) depth profiling are currently offered by the DuPont CCAS (Corporate Center for Analytical Sciences) organization and DuPont Analytical Solutions. Characteristics of the technique and the sample to be studied often determine which technique is more appropriate. These include detection limits, lateral resolution, thickness regime, and the type of chemical information required (elemental vs. functional group/oxidation vs. molecularly-specific). More recently, SIMS depth profiling with a Time-of-Flight (ToF) analyzer offers high mass resolution, spatially-resolved chemical information, and the collection of the entire mass spectrum at each depth interval. In addition, the combination of ToF-SIMS depth profiling and chemometric/multivariate methods of data analysis allows better definition and characterization of interfacial regions between layers, as well as buried defects. This has called for a reassessment of how and when the two depth-profiling techniques (ESCA and ToF-SIMS) can provide complementary information. Topics including oxidation state, organic information, and influence of different sputter sources will be discussed with examples.

AS-TuP2 Ultra-thin Titanium Films as Deuterium Storage Material; Thermal Desorption Kinetics Studies Combined with Microstructure Analysis, ***E.G. Keim***, University of Twente. MESA+ Institute, The Netherlands, *W. Lisowski*, Polish Academy of Sciences, Poland, *M.A. Smithers*, University of Twente, MESA+ Institute, The Netherlands, *Z. Kaszkur*, Polish Academy of Sciences, Poland

Thin titanium films can be applied as hydrogen storage material due to titanium hydride (deuteride) formation. However, the morphology of the Ti films, which depends strongly on the Ti film thickness, affects both the deuterium sorption and titanium deuteride decomposition properties.[1] Here we present the results of TDMS, XRD, SEM and TEM, showing adsorption-desorption properties of ultra-thin Ti films as well as surface and bulk film morphology changes due to titanium deuteride (TiDy) formation. Ti films, 10-20 nm thick, were prepared in a UHV glass system[2] at 300 K. Both volumetrically controlled deuterium adsorption and TDMS[3] monitored deuterium evolution was carried out in situ, all other analyses ex situ. It was found that ultra-thin Ti films of fine grained bulk morphology (average grain size about 10 nm) form a TiDy phase with low deuterium content ($y \leq 1.2$) after deuterium treatment at 1 Pa pressure. SEM and TEM/XRD analyses reveal a very fine grained (smaller than 8 nm) surface and bulk film morphology. TDMS heating induced decomposition of ultra-thin TiDy films proceeds at low temperature (maximum peak temperature T_m about 500 K) and its kinetics is dominated by a low energy desorption ($E_D = 0.61$ eV) of deuterium from surface and subsurface areas of the Ti film.

[1] W. Lisowski, E.G. Keim, Z. Kaszkur, M.A. Smithers, Langmuir, 2007, submitted.

[2] W. Lisowski, Vacuum, 54, 13 (1999).

[3] W. Lisowski, E.G. Keim and M.A. Smithers, J. Vac. Sci. Technol. A21, 545 (2003).

AS-TuP3 Scanning Auger Microanalysis of M316LN Alloy Used as a Superconducting Magnet Conduit Material, *H.M. Meyer III, R.M. Trejo*, Oak Ridge National Laboratory, ***S.T. Downey II***, *P.N. Kalu, K. Han*, FAMU-FSU College of Engineering

This poster presents the characterization of chemically modified 316LN used as a conduit alloy in Superconducting Outsert of the 45T Hybrid Magnet System housed at the NHMFL. The conduit material acts as a protective jacket and carrier of the Nb_3Sn superconductors formed within the magnet coil. This alloy was developed to withstand the deteriorative effects of the Nb_3Sn reaction heat treatment while maintaining high strength, toughness and ductility at liquid helium temperatures. This heat treatment, necessary for forming the Nb_3Sn superconductors within the magnet coil, is known to cause sensitization in most unmodified austenitic steel grades. Sensitization is the formation of brittle, chromium rich phases which degrade the mechanical behavior of this structural material. Cryogenic mechanical testing of M316LN upon exposure to the high temperature, long duration heat treatment (700C for 100 hours) was used to validate its current use. Mechanical tests show a significant loss in fracture toughness (~45%), although little microstructural characterization has been performed to support these findings. This poster describes our effort to provide microstructural and chemical characterization of the M316LN alloy exposed to the prescribed environments. In particular, we present scanning Auger microanalysis of the changes in chemical composition at the grain boundaries of M316LN caused by the heat treatment and resultant precipitate formation. Correlation of the Auger results with nanohardness tests at the grain boundaries will be presented. Research sponsored in part by the NSF through the Partnership for Research and Education in Materials Science under Grant No. DMR-0351770 and in part by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

AS-TuP4 Chemical Reaction of Alkali Metal with 1,3-butadiene on Si(100)2x1 Surface, ***H.Y. Park***, Korea Research Institute of Chemical Technology, *S.H. Kim, J.R. Ahn*, Sungkyunkwan University, Korea, *K.-S. An*, Korea Research Institute of Chemical Technology

The chemical adsorption of Na with 1,3-butadiene (BD)overlayer on Si(100)2x1 surface have been studied using X-ray photoelectron spectroscopy and synchrotron radiation photoemission spectroscopy in order to investigate the possibility of organic molecule-metal multilayered structure on semiconductor surface using unsaturated functional group of molecule on the top layer. As well known, the ethylene-like overlayer was induced by BD adsorption on Si(100)2x1 surface with [4+2] cycloaddition reaction (Diels-Alder reaction) at RT without breaking Si dimer. At low coverage of Na adsorption on the BD overlayer, large binding energy shift of C 1s core level spectrum was induced, which may be explained by Fermi level shift due to charge transfer from adsorbed Na to anti-π bonding state of C=C. Interestingly, the BD overlayer induces metallic Na layer beyond the RT saturation at higher coverage although Na adsorption on clean Si(100)2x1 surface has a saturation coverage (1 monolayer by double layer model) at RT. In this study, from work function changes, core level shifts, and valence band spectra, the chemical reaction of Na with ethylene-like BD overlayer on Si(100)2x1 surface are discussed.

AS-TuP5 Coding and Functionalization of Nanoparticles for Forming Photonic Bandgap Structures, *Y.-T. Kao, H.-T. Su*, ***C.-C. Chang***, National Taiwan University

Developing chemical strategies for synthesizing and characterizing functionalized nanoparticles and microspheres on which atomic aggregates of unique properties are coded for forming a lattice of repeating patterns as the photonic crystal are of great challenge for elevating photonic crystal research towards practical photonic device fabrication. When used in the photonic circuitry system, the crystal containing property-enhancing, functionalized microspheres must possess, among others, high degrees of optical clarity. This mandates high quality dispersions of the functionalized nanomaterials within the host matrix. Nanoparticles and microspheres of different chemical compositions and refractive indexes have been synthesized using a variety of chemical synthetic approaches. They were then coated with metal nanoparticles or functionalized with inorganic linkers, which were well dispersed on the surface of unit spheres. Photonic crystals were produced by self-assembly of these unit spheres through gravity or pressure. A variety of analytical methods were employed to reveal the chemical process involved in the synthesis, coding and functionalization of the unit spheres. Selective binding of species with unique functions to the surface of the unit materials was achieved by pretreating the materials surface, designing precursor molecules, and controlling the reactions involved in coding and functionalization. The bonding, reaction chemistry as well as the chemical identification of the species that were coded on the model unit materials surface will be discussed.

AS-TuP6 Addition of Surface-Modified Silsesquioxane Nanofillers for Thermal Stabilization of Polymer Thin Films, ***N. Hosaka***, *K. Miyamoto, H. Otsuka*, Kyushu University, Japan, *N. Yamada, N. Torikai*, KENS, Japan, *A. Takahara*, Kyushu University, Japan

Polymer thin films have numerous technological applications which require the homogeneous film. However, producing stable films is problematic since the polymer thin films tend to dewet from the substrates. Various approaches have been adopted to stabilize these films against dewetting, and recently, much interest has focused on the use of additives to improve the thin film stability. In this paper, polyhedral oligomeric silsesquioxanes

(POSS) were used as a nanofiller. POSS have gained considerable attention due to their organic-inorganic hybrid structure which consists of a silica cage with organic groups. The salient feature of this nanosized material is the ability to functionalize the silicon corners with a variety of organic substituents. Our previous study showed that the blending of cyclopenty substituted-POSS (CpPOSS) with the polystyrene (PS) thin films led to an inhibition of dewetting in the films.[1] Structural analyses of the films revealed that CpPOSS segregated to the film surface and film-substrate interface, and the inhibition of dewetting can be attributed to the segregation of CpPOSS, accompanying modification of the energetics and morphologies of the interfaces. However, the film with CpPOSS had a problem that its surface was roughened by the aggregation of CpPOSS. Present work is focused on the surface modification of POSS with several organic groups and PS chains to improve the dispersibility of POSS in PS films. Furthermore, the dispersion state of the surface-modified POSS in the film, especially at the surface and interface of the films, was investigated, and the relationship between dewetting inhibition and structure of the film was discussed. The dispersibility of POSS in PS films depended on the surface composition, and POSS with PS chains dispersed well in the films and also stabilized the film against dewetting.[2] Smooth surface morphology of the PS film with POSS modified by PS chains was observed by atomic force microscopy. Neutron reflectivity measurements revealed that the POSS still had the tendency to segregate to the film surface and interface even after the introduction of a PS chain on its surface, and this structure seems to be preferable for the inhibition of dewetting of the films.

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[2] K. Miyamoto, N. Hosaka, H. Otsuka, A. Takahara, Chem. Lett., 35, 1098-1099 (2006).

AS-TuP7 2 Dimensional Map of Field Emission Properties of CNT Emitters Fabricated by a Screen Printing Process, *W.H. Han*, *T.Y. Park, C.J. Kang, Y.S. Kim, J.W. Kim, Y.J. Choi*, Myongji University, Korea

The spatial uniformity and durability of field emission is one of the main issues in the carbon nanotube (CNT) field emission devices fabricated by a screen printing process. In this paper, we propose novel method to visualize field emission sites of CNT films two-dimensionally by adopting scanning probe microscopy technique and verify the conditions where the field emission of CNT emitters is spatially uniform and durable. While the anode probe with a small tip diameter of <100nm was scanned over CNT emitter surface whose dimension is 200um*200um, the field emission current was recorded through Keithley 6517A, converted into 256 grayscale level and displayed on monitor through LabView program. The anode probe was made by electro-chemically etching tungsten wire and the CNT emitter sample was fabricated by screen printing multiwall CNT whose diameter is 4-6nm and length is 1-2um on the indium-tin-oxide (ITO) glass. During scanning, the gap between W anode and ITO glass surface was maintained to be few tens of um. For the large scale imaging, we used the inertial nano positioner whose model number is ANPxyz100 made by Attocube Systems as a long range scanner. With this system, we could not only measure the emission turn-on field at fixed locations but also obtain the electron emission current map over large surface areas under constant anode voltage. We will discuss the relation between the local geometry and field emission properties of CNT emitter, and the fabrication condition of CNT emitters where the field emission is uniform and stable.

AS-TuP8 Characterization of Vertical Arrays of ZnO Nanorod by AFM, *Y. Hou*, *A. Andreev, C. Teichert,* University of Leoben, Austria, *G. Brauer,* Forschungszentrum Dresden-Rossendorf, Germany, *A. Djurisic*, University of Hong Kong, P.R. China

Solar cells made from an array of high-quality vertical ZnO nanorods filled with a light-absorbing, hole conducting polymer are promising devices for efficient low-cost solar energy conversion.[1] However, achieving full control over the growth of such nanostructures leading to proper dimensional confinement (like nanorod diameter, length, density and orientation) is still a challenging task. On the other hand, Atomic Force Microscopy (AFM) is well known as a valuable tool for nanometer scale characterization of different types of nanostructures.[2] The capabilities of AFM technique are demonstrated for the characterization of vertical arrays of various ZnO nanorods.[3] In detail, the topography of the ZnO nanorods grown on Si and ITO substrates was examined. It was found that tapping mode AFM is an appropriate tool to reveal the morphological features of vertical ZnO nanorods on the nanoscale, i.e. 3D rod shape, lateral size, average height and rod height uniformity. The results are compared with those obtained by Scanning Electron Microscopy. Moreover, by cross-sectional AFM measurements it was also established that intermediate facets appear between the top (0001) and side facets. Further, polymer coated ZnO nanorods have been investigated by AFM.

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AS-TuP9 Characterization of Ceramic Materials using Electron, Ion, X-ray, and Optical Techniques, *B.W. Schmidt*, *B.R. Rogers, J.M. Burst, R.D. Geil, M.R. George, N.D. Vora*, Vanderbilt University

Ceramic materials are widely used because of their hardness, thermal stability, and electrical properties. However, these characteristics also present issues when it comes to processing. Powder pressing is commonly used, but due to the variability in powder sizes and structures, reproducibility is difficult. Therefore, fundamental understanding of interfaces and surfaces is critical to modeling efforts. Our group uses thin film experiments to gain insight into basic mechanisms, which can then be applied to more complicated systems. We are focusing on aluminum and hafnium-based materials. Al_2O_3 is used extensively today because of its low cost and excellent protective properties. Chemical vapor deposition of Al_2O_3 typically includes trimethylaluminum (TMA), a dangerous pyrophoric compound. Dimethylaluminum isopropoxide (DMAI) is an alternative precursor that displays the same high vapor pressure that makes TMA desirable, but also shows stability as a liquid in ambient conditions. Hafnium oxide materials have received recent emphasis as high-κ replacements of silicon dioxide in CMOS devices. In addition, the borides and carbides of hafnium also can be used in high temperature applications such as hypersonic flight and atmospheric re-entry. In this work, we provide examples of how Auger electron spectroscopy, Rutherford backscattering spectrometry, time-of-flight medium energy backscattering spectrometry, X-ray photoelectron spectroscopy, and spectroscopic ellipsometry have been used to characterize these ceramics.

AS-TuP10 Room Temperature Nanoimprinting of Crystalline Poly(fluoroalkyl acrylate) Thin Films, *K. Honda*, Kyushu University, Japan, *M. Morita*, Daikin Industries, Japan, *A. Takahara*, Kyushu University, Japan

Various studies have been done on the nanofabrication of polymeric materials. However, most of the studies utilize conventional polymers and little attempt has been done for the design of polymeric materials for nanofabrication. In this study, room temperature nanoimprinting of polymer thin films will be presented. Nanoimprinting technology using compression molding of thermoplastic polymers is a low cost mass manufacturing technology and has been around for several decades.[1] The polymer used for nanoimprint experiment is Poly(2-(perfluoroocthyl ethyl) acrylate) with long fluoroalkyl group (PFA-C_8). In previous report, the authors studied wetting properties and surface molecular aggregation of PFA-C_8 thin films and clarified that PFA-C_8 showed the high water repellency because of crystaliizationof long fluoroalkyl group.[2,3] PFA-C_8 was spin-coated on the Si-wafer. The film thickness was estimated as approximately 500 nm by atomic force microscopy (AFM). The mold patterned with lines (L/S of 500 nm) was imprinted onto a spin-coated PFA-C_8 thin film under various imprinting conditions and nanoimprinting characteristics of PFA-C_8 was investigated on the basis of scanning elerctron microscopy (SEM), AFM and contact angle measurement. The line patterns were observed on PFA-C_8 film surface by AFM and SEM. In addition, PFA-C_8 film was sucessfully nanoimprinted at room temperature because of the weak interaction among rigid fluoroalkyl groups in crysatallite. The nano-textured PFA-C_8 exhibited super hydrophobicity as well as high oleophobicity. Also, line imprinted surface showed anisotropic wetting behavior. The super hydrophobicity was explained by the notion of heterogeneous wetting proposed by Cassie. In this case, the space between the solid surface and probe liquid was occupied by air and consequently the contact angle was increased.

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AS-TuP11 Short and Long-term Sputter Rate Constancy Measurements, *A.S. Lea*, *M.H. Engelhard, D.R. Baer, P. Nachimuthu*, Pacific Northwest National Laboratory

The use of ion sputtering to obtain relative and absolute depth information about surface layers and films is a common application of Auger and photoelectron spectroscopy. Accurate information about sputter rates for different materials and reproducible information for similar systems requires that the conditions of operation of an ion gun be fairly well characterized and the parameters needed to obtain reproducible sputter conditions be understood. Unfortunately, most of us do not have a good sense of how stable and reproducible our actual sputter rates are. We have undertaken a study to determine the constancy of sputtering over short and long periods of times as these determine how long of a warm-up time is necessary prior to conducting sputter rate profiles, how much variability occurs during the course of an experiment, and how often one must perform sputter rate calibrations. We have three surface analysis systems, either manually or digitally controlled, in which we are conducting these constancy measurements. We have found that for one digitally controlled system, sputter rate are fairly constant over a period of a year. In the short term, sputter rates are constant following a short warm-up time. For a manually controlled system, the sputter rate is constant over a period of days provided the settings do not change over that period of time. Determination of the long-term variability of a manually controlled system for argon ion sputtering at fixed energies is part of an on-going effort. These sputter rate constancy measurements are being conducted in a Phi Quantum 2000 XPS system, a Phi 680 Auger Nanoprobe system, and a Kratos Axis 165 multitechnique system. We will provide comparisons of sputter rate constancy for these systems over the short and long-term.

AS-TuP12 Interaction of Cobalt with Weathered Steel Surfaces Studied by XPS, ***D.L. Blanchard Jr.***, *I.E. Burgeson, G.J. Lumetta, J.R. DesChane,* Pacific Northwest National Laboratory, *G.W. Wagner*, Edgewood Chemical Biological Center

Researchers at the U.S. Army Edgewood Chemical Biological Center have developed and tested a solution for decontaminating surfaces from biological and chemical warfare agents: DECON GREEN^{TM}. Prior tests conducted at the Pacific Northwest National Laboratory (PNNL) to examine the efficacy for removal of radionuclides showed that the effectiveness of DECON GREEN^{TM} in removing Co from aged steel, though better than water, was considerably lower than that observed for other surfaces. Only about 50% of the Co could be removed from the steel surface using DECON GREEN^{TM}. In the current work, the mechanism of the Co adhesion to the steel was investigated using X-ray Photoelectron Spectroscopy (XPS). Cobalt(II) chloride ($CoCl_2$) aqueous solution was pipetted onto a weathered steel coupon and allowed to air-dry. The coupon was examined by XPS to determine the chemical state of the resulting cobalt deposit. An untreated, weathered steel coupon was examined as a control, and samples of cobalt metal foil and $CoCl_2$ powder were examined as reference compounds. The steel coupon treated with the $CoCl_2$ was rinsed with water after the initial XPS analysis, then re-examined to identify any changes in the cobalt chemical state. The coupon was then treated with DECON GREEN^{TM} and rinsed with water, and re-examined. The key observations are: 1) The cobalt on the weathered steel coupon was mainly metallic, based on the shape and position of the Co $2p_{3/2}$ XPS peak, indicating that cobalt(II) in the applied solution was reduced to metal at the surface. The appearance of shoulders on the high binding energy side of the main peak suggested the presence of a small amount of oxidized cobalt. The iron in the weathered steel coupon was somewhat oxidized before the cobalt deposition; the deposition further oxidized the iron. 2) Rinsing with water did not significantly change the shape of the Co $2p_{3/2}$ XPS peak; the shape and position still indicate mainly Co metal with some oxidized cobalt, probably a cobalt hydroxide or oxide. Rinsing oxidized all the iron metal at the surface, and greatly increased the fraction of oxygen on the surface. 3) Treating with DECON GREEN^{TM} increases the fraction of oxidized cobalt at the surface, but the majority is still metallic. The iron may undergo some additional oxidation. The DECON GREEN^{TM} treatment left carbon at the surface, probably from organic constituents.

AS-TuP13 Plasma Enhanced Chemical Vapor Deposition of Trimethylsilane on Ion Vapor and Physical Vapor Deposited Aluminum, ***P.R. Scott***, *D.M. Wieliczka*, University of Missouri - Kansas City

X-ray photoelectron spectra were obtained after each stage of a plasma deposition process with depth profiles to the aluminum layer. Spectra were obtained from Silicon wafers prior to processing; and after Argon ion plasma etching, vapor deposition of Aluminum, and DC plasma deposition of trimethylsilane. The samples were transferred under vacuum from the plasma chamber to a Kratos AXIS HS x-ray photoelectron spectrometer. Spectra were taken with magnesium K-alpha x-rays at a base pressure of 10^-9 Torr. Argon plasma etching removed carbon contamination, but left a residual oxide on the surface. Aluminum ion vapor deposition films were created at 100mTorr of Argon while physical vapor deposition films were created at a pressure of 10^-7 Torr. Results of a comparison between the ion vapor deposition and physical vapor deposition films will be presented. Various plasma deposition parameters were used to produce the trimethylsilane thin films.

AS-TuP14 Sputter Rate Determinations for Different Forms of ZnO, TiO2, and Al2O3, ***M.H. Engelhard***, *T.C. Droubay, L.V. Saraf, P. Nachimuthu, A.S. Lea,* Pacific Northwest National Laboratory, *W. Stickle,* Hewlett Packard, *C. Mathews, B. Lee, J. Kim, R.M. Wallace,* University of Texas at Dallas, *D.R. Baer*, Pacific Northwest National Laboratory

Oxide films play increasingly important roles in several modern technologies, including integrated circuits, fuel cells, and sensors. Important to the use of surface analysis techniques to characterize a variety of these materials systems is the knowledge of the sputter rates for different oxides. Since research in our laboratories and for users of the US Department of Energy’s Environmental Molecular Sciences Laboratory (EMSL) user facility involves the use of oxide films and particles, we have been building an oxide sputter rate database by examining thin films grown by oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These studies demonstrate that we can usually obtain sputter rate reproducibility of better than 5% for similar oxide films grown by OPA-MBE. However, it is well known that there are many sputtering artifacts that can occur including those due to crystal orientation, structure, or the presence of impurities. In order to examine the general applicability of the information from the epitaxial film "standards" to other materials, we are measuring the sputter rates for oxide films for a different crystal structures and/or deposition techniques. Here, we report measurements of sputter rates for ZnO, TiO2 , and Al2O3 films prepared by pulsed laser deposition, chemical vapor deposition, or atomic layer deposition. We are currently examining the dependency of density as well as crystal structure on sputter rates. X-ray reflectivity (XRR) has been used to measure the thickness and density of these films and sputter rates are measured using a PHI Quantum 2000 Scanning ESCA Microprobe. The measured sputter rates are compared to rates for known thicknesses of SiO2/Si. Work at PNNL is supported by the Department of Energy and work at UT-Dallas is supported in part by the Semiconductor Research Corporation.

AS-TuP15 Ion Beam Tuning and Optimization of Nova Ion Gun in Kratos Axis Ultra DLD Spectrometer, ***H. Piao***, *J. Chera, V. Robinson*, General Electric Co.

The first part of this study focuses on the Nova ion gun beam tuning and the resulting XPS depth profiling measurements based on a standard SiO2/Si sample under different measuring conditions (ion beam energies from 0.5-4 keV). The quantitative evaluation of depth profiles in terms of sputter rate and depth resolution is discussed in more details. Changes of topography resulting from sputtering (roughness increases with sputtering time and depth) are also given a full attention. Then we report the advantages of the "float" mode with the production of relatively high current, low energy ion beams for enhanced depth resolution. Practical application of its depth profiling at interfaces is further elucidated by a typical example: SiOxNy(40nm)/SiOxCy(300nm)/SiOxNy(40nm) thin film. Finally, the improvement of the depth resolution by rotating the sample azimuthally is demonstrated.

Applied Surface Science

Room: 610 - Session AS-WeM

Chemical Imaging at High Spatial Resolution and Nanoscale Materials

Moderator: K.G. Lloyd, DuPont

8:00am **AS-WeM1 Local Chemical Measurements with the Scanning Tunneling Microscope**, ***P.S. Weiss***, The Pennsylvania State University **INVITED**

Interactions within and between molecules can be designed, directed, measured, understood and exploited at unprecedented scales. We look at how these interactions influence the chemistry, dynamics, structure, electronic function and other properties. Such interactions can be used to advantage to form precise molecular assemblies, nanostructures, and patterns, and to control and to stabilize function. These nanostructures can be taken all the way down to atomic-scale precision or can be used at larger scales. We measure these interactions and the electronic perturbations that underly them using scanning tunneling microscopy. In these and other measurements, we collect substantial data sets in order to generate distributions with the statistics of ensemble-averaging techniques, while still retaining all the single-molecule and environmental information. This requires new automated tools for acquisition and analyses. We use molecular design, tailored syntheses, intermolecular interactions and selective chemistry to direct molecules into desired positions to create nanostructures, to connect functional molecules to the outside world, and to serve as test structures for measurements of single or bundled molecules.

8:40am **AS-WeM3 Chemical Characterisation on the Nanoscale: Imaging XPS and Scanning Auger Microscopy with Ultimate Spatial Resolution**, ***M. Maier****, T. Berghaus, D. Funneman, K. Winkler,* Omicron NanoTechnology, Germany, *N. Barrett,* CEA-DSM/DRECAM/SPCSI, CEA Saclay, France, *O. Renault*, CEA-Leti, Minatec, France

In this contribution we briefly summarize the current status of Imaging XPS (iXPS) and Scanning Auger Microscopy (SAM). Novel instrument concepts are presented, one in either field achieving ultimate resolution beyond todays limits. In iXPS a great obstacle for higher resolution is the limited X-ray brilliance in the analysis area in combination with the small electron acceptance angle of current spectrometers. Today commercial laboratory instruments are limited to approx. 3 µm resolution at best. Acquisition times as well as time for experiment set up increase unacceptably when the attempt is made to utilise this kind of resolution routinely. In particular with those instruments acquiring each image pixel sequentially by either scanning the X-ray beam or the analysis spot. We present first results of the NanoESCA instrument recently installed at LETI. A new lens concept provides a huge progress for the acceptance angle of photo electrons. This is combined with a patented abberation compensated analyser allowing the acquisition of typically 640x512 image pixels in a single shot. This offers the unique possibility to achieve sub micron image resolution routinely as well as small spot spectra from well defined areas below 1µm diameter, within reasonable acquisition times. In the field of SAM, the spatial resolution depends mainly on the performance of its electron source. Crucial parameters are the probe diameter, the electron energy, and the beam current density. As state of the art a spatial resolution on the order of 10 nm and slightly below has been demonstrated recently on the most advanced commercial instruments, using beam energies as high as 20 keV. However, the Auger cross section increases for lower beam energies and the scattering volume in the sample decreases. Thus operation at lower beam energies is desirable, but the probe diameter still shall not increase to an counteracting extent. We present SAM measurements acquired with a new electron source employing a patented lens system optimised for low beam energies and high current density. This concept enables the highest so far reported SAM resolution of 5 nm (at 10kV). Even at beam energies as low as 1keV more than 1 nA beam current can be focussed into <10nm spotsize. Furthermore we describe the combination of SEM/SAM with complementary techniques, such as STM/AFM, 4 Probe STM, SEMPA, or EBSD to provide information on topography, electronic structure, magnetic domains, or crystal orientation.

9:00am **AS-WeM4 Application of Chemical Imaging in the Pharmaceutical Industry**, ***X. Dong****, C.A.J. Kemp*, Eli Lilly and Company

Chemical imaging methods have seen increased utilization within the pharmaceutical industry due to their ability to provide insight into the composition and product performance of solid oral dosage forms. The primary imaging tools used for this type of characterization include EDS, NIR, Raman, NMR, and TOF-SIMS. This presentation will focus on the use of imaging tools for studying the detailed composition of dosage forms and packaging materials, and the inhomogeneous discoloration of API stored in USP-approved materials. Additionally, data will show that TOF-SIMS can be a pivotal tool for trouble-shooting by combining high mass resolution spectra with high spatial resolution images. The strengths and limitations of various imaging techniques (chemical and physical) will also be discussed.

9:20am **AS-WeM5 In-situ Surface Analysis by Optical Means**, ***C.M. Eggleston***, University of Wyoming **INVITED**

Understanding natural geochemical systems requires investigating fundamental reactions (adsorption, dissolution/growth, electron transfer, catalysis) at a variety of solid-solution interfaces. The availability of techniques for characterizing solid-liquid interfaces in-situ has made this task simpler. Such techniques include synchrotron-based X-ray absorption spectroscopies (e.g., EXAFS, XANES), scanning probe microscopes (STM, AFM, and their variations), and developments in Raman and IR specroscopies. Here, we explore some perhaps less well-known techniques: Optical second harmonic generation (SHG), optical waveguide lightmode spectroscopy (OWLS), and photocurrent measurements coupled to impedance spectroscopy. SHG is a nonlinear optical technique. Briefly, the interface represents a noncentrosymmetric setting between two centrosymmetric bulk phases. Intense laser light impinging on an interface can produce a few photons of doubled-frequency (second harmonic) whose intensity and polarization can be related to the concentration - and possibly orientation - of adsorbed species. We have used SHG to observe the adsorption of organic molecules to oxide surfaces and to study the structure of water near charged oxide surfaces. OWLS operates on the basis of small changes in the effective refractive index of a waveguide of sub-wavelength thickness as the result of molecular adsorption to the waveguide surface. We are using OWLS to study the adsorption of proteins, particularly outer membrane cytochromes from iron-reducing bacteria, on oxide surfaces. This technique has proven crucial in studying the adsorption of small amounts of protein. Furthermore, comparison of quartz crystal microbalance (QCM) adsorption results (which includes associated water in the adsorbed mass) to OWLS results (which excludes associated water) shows that of the total adsorbed mass, only 27% is protein in these cytochromes. Our work with semiconducting oxide electrodes necessitates electrode charcterization with regard to flatband potential, charge carrier density, and other properties. In addition, these and photocurrent transient techniques allow us to locate electronic states both at the semiconductor surface and within its bulk bandgap. This presentation will briefly show how such states may be located and studied using photocurrent transient spectroscopy and impedance spectroscopy in the case of iron oxide photocatalysts.

10:40am **AS-WeM9 Synchrotron Radiation Induced X-ray Photoelectron Emission Microscopy (SR-XPEEM) with Aberration Corrected Energy Filterin**, ***N. Barrett***, CEA-Saclay, FR, *O. Renault,* CEA LETI Minatec, FR, *L.-F. Zagonel,* CEA Saclay, FR, *A. Bailly,* CEA LETI Minatec, FR, *J. Charlier, J. Leroy,* CEA Saclay, FR, *J.C. Cezar, N. Brookes,* ESRF, FR, *M. Senoner,* Fed. Inst. Mtls Testing, Germany, *J. Maul, T. Berg, F. Schertz, G. Schönhense*, Univ. of Mainz, Germany

The combination of high brightness photon source and aberration corrected energy filtering has allowed new progress in the field of electron emission microscopy for nanoscience and nanotechnology. The first commercially available NanoESCA instrument (OMICRON GmbH) has been recently commissioned and tested at the CEA Nanocharacterization centre (Minatec) in Grenoble and on beamline ID08 at the ESRF. We first present the principles of spectromicroscopy, and in particular the use of an electrostatic PEEM column together with an energy aberration corrected double hemispherical analyzer. The objective immersion lens and the high extraction voltage considerably improve lateral resolutions. The use of a contrast aperture reduces the chromatic aberrations in the PEEM column. The accurate focus tracking of the instrument allows imaging at the secondary electron threshold and across specific core levels at chosen kinetic energies. The resulting lateral resolution better than 150 nm and energy resolution give an imaging capability with full chemical state sensitivity. The principles will be illustrated by several examples. The core level intensity contrast is demonstrated with a multilayer certified standard sample of GaAs/GaxAl1-xAs variable multilayer. The energy resolved chemical mapping will be illustrated via the preferential molecular grafting on a heterogeneous Au-Si substrate. Finally, the depth resolution thanks to the variable photoelectron escape depth is employed to do non-destructive position detection of pre-solar grains coming from a meteorite, prior to nano-SIMS analysis. The perspectives include reaching the ultimate resolution limits using an optimized synchrotron beamline, the development of valence band imaging and the study of single nanodevices.

11:00am **AS-WeM10 Directed Growth of Ordered Metal Nanostructures on Crystalline Cellulose Templates*, G.J. Exarhos*,** *Y. Shin*, Pacific Northwest National Laboratory

A form of nano-crystalline cellulose, isolated from carbohydrate-derived materials like paper or cotton, serves as a reducing template that drives formation of ordered regions of metal nanoparticles or nanorods when placed in aqueous metal precursor solutions under hydrothermal conditions. Uniform sized gold, silver, palladium, platinum, copper, nickel, selenium and other metal or metal-oxide nanocrystals were observed to rapidly nucleate and preferentially grow along the ordered hydroxyl-rich regions of the substrate. The ordered metals display catalytic, electrical and optical properties that would not normally be present in larger crystals. For example, a marked enhancement in the rate of degradation of organic dyes in water under uv-irradiation has been measured when selenium-decorated templates were immersed in methylene blue solutions. Materials have been characterized by means of XRD, FESEM, TEM, and optical methods. The mechanistics of the growth process will be discussed based upon these structural measurements and the known reducing properties of carbohydrate materials. Prospective uses of these materials for catalysis and in optical applications also will be described.

11:20am **AS-WeM11 Critical Issues Concerning the Use of Nanomaterials In Aerospace Platforms*, P.T. Lillehei***, NASA Langley Research Center **INVITED**

Revolutionary aerospace vehicle designs are enabled by the use of lightweight structural composites. These composites must possess structural integrity and multifunctionality features, such as lightning strike protection, for the vehicle to fully realize the weight savings. NASA and the aerospace industry are aggressively pursuing the use of nanomaterials as both structural reinforcements and as an enabler of multifunctionality. Optimal utilization of nanomaterials in multifunctional aerospace platforms will demand an understanding of the fundamental principles that govern their behavior at the nanoscale. For example, NASA has established that a critical factor governing the electrical conductivity characteristics of a nanomaterial or nanocomposite is the degree of dispersion of the nanomodifier in the host matrix. However, before conductive nanomaterials can be considered for use in applications such as lightweight, flexible, surface mountable materials for lightning strike protection, a set of robust, field- ready quality assurance/control (QA/QC) standards must be developed. The research described in this presentation establishes a means of quantifying the dispersion of carbon nanotubes in high-performance, aerospace polymers. Work can now begin on developing the field ready QA/QC implementations of these techniques.

12:00pm **AS-WeM13 Functionalization and Characterization of Gold Nanoparticles*, S.D. Techane*,** *L.J. Gamble, D.G. Castner*, University of Washington

Gold nanoparticles (AuNPs) are non-toxic and have a high percentage of surface atoms, which gives them special electronic properties and reactivities. Since these properties are dependent on the size, shape and surface chemistries of the AuNPs, one can vary these quantities to achieve desirable applications for AuNPs in biomedicine, microarray and biosensor fields. In this research, AuNPs of different diameters (14nm - 50nm) were synthesized with a citrate reduction method and later functionalized with various chain lengths (3, 6, 8, 11, and 16 carbon chain) of carboxyl terminated alkyl thiol by direct displacement of the citrate ions. To obtain a hydrophobic surface, functionalization with 1-dodecanethiol was tried using a two step functionalization method. The size, shape, and size distribution of the AuNPs were characterized with transmission electron microscopy (TEM) and ImageJ, where the distribution in terms of 3 σ ranged from 2.5 to 20nm, depending on the average diameter of the AuNPs. Surface chemistries of the self assembled monolayer (SAMs) of alkyl thiol were analyzed with X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry. Comparison between SAMs of 16-mercaptohexadecanoic acid (C/O = 8 and C/S = 16) on AuNPs and flat Au surface was done to verify the applicability of XPS data analysis method for curved nanoparticle surfaces. Surface atomic composition ratios: C/S (26 for AuNPs and 42 for flat Au), C/O (5 for AuNPs and 8 for flat Au), C/Au (1.7 for AuNPs and 1.2 for flat Au) exhibited some differences between the two surface types. These differences indicate the need to develop specific XPS data analysis methods to accurately represent the surface chemistries of curved nanoparticles surfaces. XPS results for the two-step functionalization method, which uses thioctic acid as an intermediate, showed 11% oxygen surface composition with 6% carboxyl carbon indicating incomplete displacement of the intermediate carboxyl thiol and a need for a better functionalization method to achieve hydrophobic surface. AuNPs with carboxyl terminated SAMs are being used to investigate adsorption thermodynamics of short chain peptides onto these surfaces. Protein assay, XPS, and NMR are being used to characterize the adsorbed peptides.

Applied Surface Science

Room: 610 - Session AS+BI+NS-WeA

Fabrication and Characterization of Functional Soft Material Surfaces

Moderator: R.T. Haasch, University of Illinois at Urbana Champaign

1:40pm **AS+BI+NS-WeA1 UPS Work Function Measurements on Polymers Combined with C60 Depth Profiling**, ***S. Raman***, *J. Moulder, J.S. Hammond,* Physical Electronics, *N. Sanada, M. Suzuki*, ULVAC-PHI, Inc.

The performance of ultra thin organic films in organic LED's (OLED) is dependent on the work functions of the electrodes and polymers forming the OLED junctions. Historically, the work functions have frequently been derived from the secondary electron emission edges measured with UPS. The recent applications of C60 ion beams for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage, have offered a new tool for studying surface modified polymers. By combining these two techniques, the work function and composition as a function of depth of polymers targeted for OLED applications can be characterized by XPS and UPS. The surface characterization of OLED component polymers exposed to deleterious environments will also be discussed. The possible chemical surface damage induced by the C60 ion beams will be examined by both XPS and UPS spectra and secondary electron emission edge spectra.

2:00pm **AS+BI+NS-WeA2 Patterning and Bonding of Poly(dimethylsiloxane) A Simple New Method for Creating Optically Transparent Biocompatible Surfaces and Robust Microfluidic Devices**, ***P.R. Norton***, *N. Patrito, J. McLachlan, J. Chan, S. Faria, S. Tadayyon*, University of Western Ontario, Canada

Our group has developed a simple protocol to prepare inexpensive, single-component substrates capable of confining cell attachment and growth. In the presence of an argon plasma, thin metal films are deposited onto poly(dimethylsiloxane) (PDMS). Removal of the metal layer exposes regions of the polymer surface that are enriched in oxygen and promote the adhesion of fibroblast, epithelial and myoblast cells. This method produces bioactive arrays of controlled size (down to scales in the order of µm), shape, pitch and symmetry on which cells can be grown to confluency. The treated material is storable and can be activated just before use; this eliminates stability problems inherent in a number of previously reported PDMS surface treatments, most notably oxygen plasma modification. The patterned arrays offer highly adaptable means to probe cell-cell interactions, cell motility and cell signaling in response to varied spatial or geometric organization and they are being incorporated into microfluidic channels for combined optical and proximal probe studies of live cells. Serendipitously, this surface treatment alters the mechanical properties of PDMS, rendering the modified material sensitive to tensile stresses imposed by cells. Cellular traction forces generate nanoscale ripples in the elastic substrata which extend outward from the cell bodies and which can be imaged by dark-field microscopy and AFM. Detailed analyses of these ripples can potentially provide a direct measure of cellular traction forces and mechanical signaling. In related experiments, we have also developed a novel means of bonding PDMS to a host of materials relevant to microfluidic device fabrication, including glass, Si, SiO2 and polystyrene. To quantify the adhesive strength, closed PDMS-glass and PDMS-PDMS microfluidic devices were fabricated and subjected to tensile and leakage testing. The data indicate a significant improvement in performance over previously reported bonding technologies, resulting in the production of more robust, longer-lasting microfluidic devices and the concomitant possibility of using higher pressures and flow-rates.

2:20pm **AS+BI+NS-WeA3 Interfacial Structure of Polymer Brush and Gel Investigated by Sum Frequency Generation Spectroscopy**, ***K. Uosaki***, *H. Noguchi, S. Nihonyanagi, H. Minowa, R. Yamamoto*, Hokkaido University, Japan

Polymer brush and gel plays very important roles in biological systems. Information on the interfacial structure is essential to understand the function of these materials. Here we employed sum frequency generation (SFG) spectroscopy, which is known to possess high surface specificity, to investigate the molecular orientation/conformation of polymer brush under various environment and water structure at PVA gel/solid interface. SFG spectra of alkylated poly (vinyl pyridine) in contact with dry nitrogen, water vapor, and liquid water were obtained. The peaks due to CH vibration of CH3 dominated in nitrogen, showing that the side chains are highly ordered. When the polymer layer is in contact with water vapor, in addition to the two peaks due to CH3 group, two peaks of CH2 group were observed, indicating that many gauche defects existed. The SFG spectrum of the polymer brush in contact with liquid water showed no peaks in CH stretching region except for small shoulder due to the ring CH modes, indicating the alkyl side chain was completely disordered. SFG spectra of the polymer brush in OH stretching region were also obtained. A broad band assigned to the OH stretching was observed in water vapor. Two bands corresponding to the OH stretching of the interfacial water molecules at 3200 cm-1 due to "ice-like water" and at 3400 cm-1 due to "liquid-like water" dominated in liquid water. Poly vinyl alcohol (PVA) gel is considered to be one of the possible candidates for an artificial articular cartilage in artificial joints because of very low friction between PVA gel and solid. SFG measurement proved that while the fractions of the "ice-like" and "liquid-like" water were almost equal at water/quartz interface, the fraction of the "liquid-like" water became much higher when the PVA gel was pressed against the quartz surface, showing that the weakly hydrogen bonded water dominate at PVA gel/quartz interface where friction is very low. SFG measurement in Ar showed only weakly hydrogen bonded water was present at the PVA gel/quartz interface. The effect of PVA gel contact was less obvious at the octadecyltrichlorosilane (OTS) coated quartz, where the friction is much higher. These results suggest the important role of weakly hydrogen bonded water for very small friction at PVA gel/solid interface. In conclusion, SFG is demonstrated to be a very useful technique to characterize molecular structure at solid/liquid interfaces including biological interfaces.

2:40pm **AS+BI+NS-WeA4 Multiphoton Patterning of Planar and Topographically Complex Surfaces for Control of Photon, Electron, and Chemical Transport**, ***P.V. Braun***, University of Illinois at Urbana-Champaign **INVITED**

Multiphoton patterning enables fabrication of complex structures with minimum feature sizes on the order of the volume of the focal point. Using a pulsed laser source coupled to a laser scanning confocal microscope, we have concurrently written and imaged various complex structures and patterns. Recently, along with formation of complex structures, we have initiated efforts to locally modify the surface chemistry of both planar and topographically complex (three-dimensional) surfaces to create pathways for photon, electron, and chemical transport. A series of organic chemistries have been developed to enable this patterning, which revolve around the grafting of photoswitchable molecules or polymer brushes to the various surfaces. Once the local chemistry of the surface has been modulated, this chemistry can be amplified through quantum dot attachment, electroless plating, or surface initiated polymerization to create two and three-dimensional patterns for control of photon, electron, and chemical transport. Colloidal crystals and porous glasses are used as model three-dimensional substrates; standard materials are used for two-dimensional structures.

4:00pm **AS+BI+NS-WeA8 Chemical Modification of Self-Assembled Monolayer Surfaces using Soft-Landing of Mass-Selected Ions**, ***P. Wang***, *O. Hadjar, J. Laskin*, Pacific Northwest National Laboratory

Stable immobilization of peptides on solid supports plays an important role in biochemistry. Existing techniques for linking peptides to surfaces are based on a variety of solution-phase synthetic strategies and require relatively large quantities of purified material. Here, we report a novel approach for preparation of peptide arrays on self-assembled monolayer (SAM) surfaces using soft-landing (SL) of mass-selected ions. This approach takes advantage of the exceptional selectivity in preparation of projectile ions by mass spectrometry. We demonstrate efficient reactive landing (RL) of several model peptides onto the SAM of N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM). This method introduces unprecedented selectivity and specificity into the surface preparation step by eliminating the effect of solvent and sample impurities on the quality of the film. Peptide ions produced by electrospray ionization are mass-selected and deposited onto SAM surfaces using a novel ion deposition chamber designed and constructed in our laboratory. NHS-SAM, which readily reacts with accessible primary amino groups in proteins or peptides by forming amide bonds, is used as a target for soft-landing experiments. Freshly prepared SAMs and modified surfaces are characterized ex situ using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and infrared reflection absorption spectroscopy (IRRAS). Mass-selected ions of model peptides including cyclo(-RGDfK-), GRGDSPK and RGDGG were soft-landed onto the NHS-SAM surface.

ToF-SIMS and IRRAS characterization suggested efficient covalent binding between the two lysine-containing peptides and the NHS-SAM by the formation of an amide bond through the lysine side chain. Systematic studies were carried out to understand the factors that affect the efficiency of reactive landing. We found that the reaction takes place upon collision and is promoted by the kinetic energy of the ion. The reaction yield is independent of the charge state of the projectile ion suggesting efficient neutralization of peptide ions upon collision. Chemical reactivity and physical properties of the SAM surface are also important factors that affect the outcome of RL. RL of mass- and energy-selected peptide ions on surfaces provides a highly specific approach for covalent immobilization of biological molecules onto SAM surfaces.

4:20pm **AS+BI+NS-WeA9 TOF-SIMS Analysis of Polypropylene Films Modified by Isotopically Labeled Methane Flames**, ***S.J. Pachuta***, *M.A. Strobel*, 3M Company

Flame treatment is a common industrial process for modifying polymer surfaces. Surfaces exposed to flames are known to oxidize, but studies of the oxidation mechanism have been largely confined to correlating simple surface properties with models of the flame composition due to the lack of direct experimental data on the flame-surface interaction. In this work, polypropylene film surfaces were oxidized by exposure to a flame fueled by isotopically-labeled methane (CD_4). The isotopic sensitivity of time-of-flight secondary ion mass spectrometry (TOF-SIMS) was then used to gain new insights into the mechanism of flame treatment. TOF-SIMS analysis indicates that much of the oxidation of polypropylene occurring in fuel-lean flames is not accompanied by deuteration, while for polypropylene treated in fuel-rich flames, deuteration is extensive, and some of the affixed oxygen is deuterated. These observations imply that O_2 is the primary source of affixed surface oxygen in fuel-lean flame treatments, but that OH may be a significant source of affixed oxygen in fuel-rich flame treatments. Application of principal component analysis (PCA) and multivariate curve resolution (MCR) to the TOF-SIMS data was found to provide information beyond that which could be obtained by traditional peak-ratio methodology.

4:40pm **AS+BI+NS-WeA10 The Analysis of Oxidation Profiles in Elastomers Using ToF-SIMS**, ***J.A. Ohlhausen***, *M.C. Celina, M.R. Keenan*, Sandia National Laboratories

As elastomeric materials age, their mechanical properties can change such that they do not perform their desired function. It is important to understand the aging behaviour of such elastomers, so that predictive aging models can be developed. In that light, much work has been done to understand oxygen diffusion limited aging processes under accelerated aging conditions for a range of elastomers.[1-2] In these studies, mechanical properties as a function of depth were determined under differing temperature/time conditions. In addition, chemical changes were measured by analyzing microtomed sections using FTIR. Unfortunately, these measurements were difficult to perform on carbon-black filled samples and were also relatively time consuming. Ideally, an alternative method is needed to measure the chemical oxidation profiles of commercial o-rings containing fillers in a quick and efficient manner. In this talk, the usefulness of ToF-SIMS as a technique to measure the position-dependent extent of oxidation in filled elastomers will be discussed. Accelerated aging in 18O is used to demonstrate the ability of SIMS to directly measure the extent of oxidation. Examples of 18O- cross section line scans in aged elastomers will be discussed and compared to known diffusion limited degradation mechanical profiles. It will be shown that filled elastomers can be analysed using these methods. Additionally, the ability to measure oxidation profiles in air-aged samples will also be shown. Thus, ToF-SIMS is seen as a rapid evaluation tool for the measurement of elastomer oxidation for engineered elastomers. The benefits and limitations of the technique will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

[1] M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, Polymer Degradation and Stability 60 (1998) 493-504

[2] M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, Polymer Degradation and Stability 68 (2000) 171-184 .

5:00pm **AS+BI+NS-WeA11 Surface Chemical Analysis of Nano-Scaled r.f. Plasma Polymer and Co-Polymer Films by using a Combination of "In-Situ"and Ex-Situ Characterization Tools: Hydroxylated and Aminated Surfaces by XPS, ToF-SIMS and NEXAFS Spectroscopy**, ***W.E.S. Unger***, *A. Lippitz, S. Swaraj, E. Yegen*, Federal Institute for Materials Research and Testing (BAM), Germany

The formation of plasma-polymerized materials made from organic molecules is a technologically highly attractive way to obtain films with unique properties. Surface properties like bio-compatibility, wettability, etc., can be adjusted by tailoring the chemical functionalization. A controlled deposition of those films requires the development of surface analytical procedures which are able to derive useful information on relevant parameters. This can be a hard job for an analyst because plasma-polymerized or plasma-modified materials are extremely complex samples. Their complexity is caused by the co-existence of a relatively high number of chemical species. This leads to a kind of mixture analysis at surfaces but without the possibility of a separation step as it is possible, e.g., by using GC-MS techniques in the analysis of organic mixtures. Relevant parameters for film characterization are primarily (1) qualitative and (2) quantitative determination of functional groups. However there are other important parameters as for instance (3) the cross-linking and branching within the films or even the concentrations of (4) radicals and (5) unsaturated species in the films. It is well known that plasma-polymerized materials may undergo ageing processes. It is assumed that many of them will be initiated by radicals in the films. These radicals are inherently produced by plasma processing. Approaches have to be developed enabling a study of ageing processes on the molecular level including the respective reaction kinetics. So-called "in-situ" techniques of surface chemical analysis are required to investigate the real fresh state of samples. Using a selection of hydroxylated or aminated model plasma polymers and co-polymers it will be demonstrated how analytical approaches based on a combination of photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and x-ray absorption spectroscopy (XAS) may provide solutions for the analytical challenges summarized above.

Biomaterial Interfaces

Room: 609 - Session BI+AS+NS-ThA

Surface Analysis and Related Methods for Biological Materials

Moderator: S.L. McArthur, University of Sheffield, UK

2:00pm **BI+AS+NS-ThA1 Creating and Probing Model Biological Membranes**, ***S.G. Boxer***, Stanford University **INVITED**

During the past few years, our lab has developed a wide range of methods for patterning lipid bilayers on solid supports.[1] These 2D fluids are interesting both as a model for biological membranes and as a physical system with unusual properties. Methods have been developed for controlling the composition of patterned membrane corrals by variations on microcontact printing and microfluidics. Charged components can be moved around within these fluid surfaces by a form of 2D electrophoresis. The planar geometry of supported bilayer systems is ideal for high resolution imaging methods. The lateral (x-y) composition of membranes can be analyzed by high spatial resolution secondary ion mass spectrometry (SIMS) using the NanoSIMS 50 (Cameca) at the Livermore National Laboratory. Results will be described for simple membrane compositions[2] and phase separated domains[3] suggesting the potential of this method for the analysis of membrane organization in complex membranes. Extensions of this approach to more complex systems including membrane-associated proteins will be described. If time permits, a complimentary optical imaging method offering sub-nm resolution in the z-direction (perpendicular to the membrane surface) will be described in the context of imaging conformational changes in membrane proteins.

[1] J. T. Groves and S. G. Boxer, Accounts of Chemical Research, 35, 149-157 (2002).

[2] C. Galli Marxer, M. L. Kraft, P. K. Weber, I. D. Hutcheon and S. G. Boxer, Biophysical Journal, 88, 2965-2975 (2005).

[3] M. L. Kraft, P. K. Weber, M. L. Longo, I. D. Hutcheon, S. G. Boxer, Science, 313, 1948-1951 (2006).

2:40pm **BI+AS+NS-ThA3 Activation Thermodynamics for Phospholipid Flip-Flop in Planar Supported Lipid Bilayers Measured by Sum-Frequency Vibrational Spectroscopy**, ***T.C. Anglin***, *H. Li, J.C. Conboy*, University of Utah

Basic transition state theory is used to describe the activation thermodynamics for phospholipid flip-flop in planar supported lipid bilayers prepared by the Langmuir-Blodgett / Langmuir Schaeffer method. Kinetics of flip-flop are determined as a function of varying temperature and lateral surface pressure for model bilayers of 1,2-distearoyl-sn-glycero-3-phosphocholine (DSPC) using sum-frequency vibrational spectroscopy (SFVS). The temperature and pressure dependence of the kinetics of DSPC flip-fop provide a complete description of the activation thermodynamics for flip-flop in the gel state, including free energy of activation, area of activation, and entropy of activation. This is the first description of phospholipid flip-flop according to basic transition state theory with explicit treatment of the free-energy dependence of the process and determination of the entropic contribution to the transition state.

3:00pm **BI+AS+NS-ThA4 Observation of Electrical Characteristics at Cells Membrane using by Electrostatic Force Microscopy**, ***Y.J. Kim***, Myongji University, Korea, *H.D. Kim,* Seoul National University, Korea, *Y.S. Kim,* Myongji University, Korea, *K.H. Lee,* Seoul National University, Korea, *C.J. Kang*, Myongji University, Korea

Recent advances in atomic force microscopy (AFM) made it possible to investigate the biological materials in a single molecule level. Moreover, the AFM has been used to measure the fine structure of individual live cell even under physiological liquid. The images of cells measured show finer structure of cell boundary compared with those of SEM after fixation. Since electrostatic force microscopy (EFM) using conducting cantilever to AFM allows us to observe the electrical properties of the surface, it is also used to study the various properties of the cell membrane. Reportedly, it is known that protein expression depends on the cell kinds and shows the non uniform distributions, which causes the electrical potential difference on the cell surface in the local area. Thus mapping the electrical potential of a cell using EFM and comparing it with that of reference group, we are able to extract the information to differentiate the cells. In this work, we have identified the breast cancer cells (MCF7) and normal breast epithelial cells (MCF10A) derived from the same origin by fractal dimension analysis using AFM and the electrical properties of the cell membrane measured from the EFM will be also discussed. The results show that AFM imaging with EFM measurement might be feasible methods for analyzing surface structures of living cells with high resolution, and it could provide new insights into cell surface structure.

3:40pm **BI+AS+NS-ThA6 Two and Three Dimensional Analysis of C. Albicans Biofilms with Cluster SIMS**, ***B.J. Tyler***, *S. Rangarajan,* University of Utah, *J. Moeller, H.F. Arlinghaus*, University of Muenster, Germany

The high tolerance of microbial biofilms to important antimicrobial agents creates an import problem for treatment of infections associated with implanted medical devices. Several important hypotheses for this drug resistance involve mass transport limitation within the biofilms. We have been using 2_D and 3_D ToF-SIMS analysis to investigate transport of drugs and nutrients through C. albicans biofilms. Analysis has been performed using a novel ToF-SIMS system which incorporates a cryo-sectioning chamber and precise temperature control during analysis. This instrument has allowed us to map the distribution of key nutrients and drugs with in the biofilm as well as to identify viable vs. nonviable cells. Through these studies, we have determined that the multiple cellular layers and extracellular polymers are not the most important mass transport barrier. Common drugs are able to permeate to the bottom of the biofilm within 5 minutes but are still unable to penetrate the cell wall of persister cells found at the base of the biofilm. Current work is focusing on cell wall and membrane changes within a subpopulation of the biofilm cells which apparently limits transport of antimicrobials into the cells. Multivariate statistical techniques have been crucial for the analysis of these samples and discussion of the relevant statistical methods employed will be presented.

4:00pm **BI+AS+NS-ThA7 XPS, ToF-SIMS and NEXAFS Investigation of Peptide Adsorption onto SAMs**, ***J.S. Apte***, *L.J. Gamble, D.G. Castner*, University of Washington

The interactions between proteins and surfaces are critical to the success or failure of implants in the body. When adsorbed onto a synthetic surface, proteins often denature which can trigger the foreign-body response. It is therefore essential to develop methods to examine these interfacial phenomena. This work uses X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS) and near-edge X-ray absorption spectroscopy (NEXAFS) to characterize the structure of α-helix and β-sheet peptides adsorbed onto self-assembled monolayers (SAMs). The α-helix peptide is a 14-mer made up of lysine (K) and leucine (L) residues with a hydrophobic periodicity of 3.5. The β-sheet peptide is a 15-mer also made up of L and K residues with a hydrophobic periodicity of 2. A β-sheet peptide with the same structure but with valine (V) substituted for L was also studied since V has a higher tendency than L to form β-sheet structures. All peptides have the hydrophobic side-chains on one side of the peptide and the hydrophilic on the other. The SAMs studied were thiols on gold containing the ω-groups $-CH_3$, -OH, -COOH, $-NH_3^+$ and $-CF_3$. XPS nitrogen atomic percent was used to measure adsorption isotherms for the peptides. The α-helix peptide forms a monolayer (8.2% N) on the COOH-terminated SAM at an adsorption concentration 50 times lower than on the CH_3-terminated SAM (0.01 mg/mL compared to 0.5). The surface coverage on the CH_3 SAMs appeared to be patchier compared to the COOH SAMs, since they had standard deviations of 2-3% N. Atomic force microscopy images of the adsorbed peptides were generated to examine this patchiness. Also, the adsorption process depended on buffer salt concentration. Little peptide adsorption was detectable on the methyl SAMs when adsorbed from a 0.1x buffer. ToF-SIMS was used to investigate the ratio of K to L characteristic mass fragments at 84 and 86 m/z, respectively. The 84/86 (K/L) ratio on CH_3 SAMs (1.2) was the same, within experimental error, as the ratio on COOH SAMs (1.1). Polarization dependent NEXAFS experiments at the nitrogen K-edge indicated the β-sheet was lying down on the SAM surfaces. The α-helical peptide exhibited significantly less polarization dependence than the β-sheet peptide, probably due to the different structure of the backbone amide groups in the α-helical peptide.

4:20pm **BI+AS+NS-ThA8 Isolation and Detachment of Small Cell Populations from a Thermoresponsive Polymer**, ***H.E. Canavan***, *K. Gallagher-Gonzales, J.A. Reed*, University of New Mexico

Poly(N-isopropyl acrylamide) (pNIPAM) has proven to be an efficient and non-destructive means of detaching intact sheets of mammalian cells. In addition, cell sheets detached from pNIPAM maintain their association with the extracellular matrix (ECM) during and following detachment from a coated surface, enabling their use in tissue engineering. To date, the majority of those studying cellular interactions with pNIPAM have focused on harvesting large domains of cells for such tissue engineering applications. However, there are many other applications for which the non-destructive release of smaller populations, or even isolated cells, is desirable. For example, isolated cells are required to ascertain the extent of transmembrane protein receptor upregulation when assaying the efficacy of cancer therapeutics on cell populations via flow cytometry (FC). In this work, arrays of thermoresponsive domains were fabricated to isolate defined populations of cells using a variety of techniques. The surface chemistry, thermoresponse, and topography of the films generated were verified via X-ray photoelectron spectroscopy (XPS), contact angle measurements, and atomic force microscopy (AFM), respectively, and compared to controls. The cell releasing properties of the films were characterized by incubating baby hamster kidney (BHK) and bovine aortic endothelial cells (BAECs). The behavior of the cells from isolated cells and small cell populations were characterized and compared to large cell population controls.

4:40pm **BI+AS+NS-ThA9 Surface Characterization of Ordered Nanopatterns made from Self-Assembly of Mixed Nanoparticles**, *S. Pillai, G. Singh,* The University of Aarhus, Denmark*, C. Blomfield, A. Roberts,* Kratos Analytical Ltd, UK*, R.L. Meyer,* ***P. Kingshott***, The University of Aarhus, Denmark

Controlled patterning of surfaces with different chemistries and structures at nanoscale length scales is highly desirable for understanding the fundamental mechanisms of protein and cell interactions with biomaterials. The use of nanoparticles (NPs) to pattern surfaces by colloidal lithography or templating using one type of NP is well known for applications such as biosensors,[1] biomaterials[2] and tissue engineering.[3] We demonstrate that by using mixed nanoparticles unique highly-ordered patterns can be obtained by simple self-assembly from buffer onto hydrophobic surfaces from both concentrated and dilute two-component NP suspensions.[4] The new method uses suspensions of poly(styrene) (PS) NPs of different size (d = 500 to 60nm) with different NP ratios and volume fractions. The ordering is independent of the NP surface chemistry (sulfated, carboxylated, or aminated PS) or zeta potential and occurs over a broad pH range (4-10). The method is demonstrated for two types of hydrophobic surfaces, a commercial adhesive carbon tape and octadecyltrichlorosilane (OTS)-modified glass where patterns of hexagonally packed large particles are inter-dispersed with smaller particles. However, very poor ordering is achieved using gold, mica and HOPG (highly oriented pyrolytic graphite) as substrates. The morphologies of the nanoparticle assemblies are characterised extensively by SEM and AFM. In addition, XPS and ToF-SIMS are used to characterise the surface chemistry of the NP surfaces, which also provides knowledge of the mechanisms of NP assembly by showing that the ordering is most likely associated with charge screening by buffer salts resulting in an entropically driven assembly process. These preliminary results indicate that use of two component NP assemblies opens up the possibilities of decorating surfaces with well-defined chemical nanopatterns capable of selective attachment of different proteins and/or protein resistant molecules.

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[3] S.N. Bhatia , U.J. Balis, M.L. Yarmush, M. Toner, FASEB J. 1999, 14, 1883.

[4] R. Mukhopadhyay, O. Al-Hanbali, S. Pillai, A. Gry Hemmersam, R.L. Meyer, C.A. Hunter, K.J. Rutt, F. Besenbacher, S.M. Moghimi, P. Kingshott, submitted.

Applied Surface Science

Room: 4C - Session AS-ThP

Aspects of Applied Surface Science II Poster Session

AS-ThP1 DNA Microarrays to Detect the Serotype of Dengue Viruses in a Large Number of Samples from Mosquitoes or Patients Collected in Mexico , *A. Diaz-Badillo,* CINVESTAV-IPN, Mexico, ***V. Altuzar***, Universidad Veracruzana, Mexico, *J.G. Mendoza-Alvarez,* CINVESTAV-IPN, Mexico, *A. Cisneros,* Universidad Autonoma Benito Juarez, Mexico, *F. Jimenez-Rojas, J.P. Martinez-Muñoz,* Salud Pública y Servicios de Salud de Oaxaca, Mexico, *J.L. Herrera-Perez,* CICATA-IPN, Mexico, *C.O. Mendoza-Barrera,* Universidad Veracruzana, Mexico, *F. Sanchez-Sinencio, P. Gariglio-Vidal, M.L. Muñoz*, CINVESTAV-IPN, Mexico

Dengue is a mosquito-borne viral infection causing a major public health problem globally. Dengue virus (DENV) is the causative agent of dengue fever and dengue hemorrhagic fever and includes four distinct serotypes (DEN-1, DEN-2, DEN-3, and DEN-4). DEN-2 and DEN-3 have been associated with severe dengue disease. In this work we demonstrated a high throughput of microarrays for detection of dengue virus in serum samples from patients with a defined dengue infection from Oaxaca or in mosquito population collected across eighteen Mexican states. We have applied microarray analysis for simultaneous serotyping multiple RNA samples from human or mosquitoes through the NS3 genome. The proposed microarray method can be used for i) rapid and reliable dengue diagnosis; ii) serotyping and iii) surveillance of mosquitoes infected with dengue. Moreover by using these microarrays we have determined DEN viruses in pools of gravid females mosquitoes collected in several sites of eighteen Mexican states in 2005. Our microarrays were also useful to confirm the presence of DEN-2 in 96 serum samples, DEN-3 in three samples from Oaxaca city and one case from Juchitán, Oaxaca contained DEN-2 and -3. The microarrays quantification were validated by using RT-PCR, in fact they presented agreement in all cases excepting with those mosquito samples collected in one site of Chiapas, Oaxaca, Morelos and Nayarit. In conclusion, we show the success of applying microarrays assay to provide a consistently robust qualitative detection of dengue serotypes (DEN-1, DEN-2, DEN-3 and DEN-4) in serum samples from patients or in pools of gravid female mosquitoes collected in the field of eighteen Mexican states.

AS-ThP2 Surface Engineering with Functional Soft Materials, ***M. Yan***, Portland State University

Organic and polymeric materials are effective in tailoring the chemical and physical properties of the surface layer, and to introduce functions to materials. We have developed a simple and versatile method for attaching a wide range of soft materials on solid substrates. The technique employs a photochemical coupling chemistry that is fast, efficient, and is capable of creating structures with control over density and topography.[1] Applications of this surface functionalization technique for the fabrication of nanowells,[2] carbohydrate microarrays[3] and single polymers[4] will be highlighted.

[1] Liu, L.; Engelhard, M. H.; Yan, M. "Surface and Interface Control on Photochemically Initiated Immobilization", J. Am. Chem. Soc. 2006, 128, 14067-14072.

[2] Yan, M.; Bartlett, M. "Micro/Nanowell Arrays Fabricated from Covalently Immobilized Polymer Thin Films on a Flat Substrate," Nano Lett. 2002, 2, 275-278.

[3] Pei, Z.; Yu, H.; Theurer, M.; Walden, A.; Nilsson, P.; Yan, M.; Ramström, O. "Photogenerated Carbohydrate Microarrays", ChemBioChem 2007, 8, 166-168.

[4] Liu, L.; Yan, M. "A General Method for the Covalent Immobilization of Single Polymers," Angew. Chem. Int. Ed. 2006, 45 (37), 6207-6210.

AS-ThP4 A Quantitative Model Relating Interphase Chemistry and Adhesive Fracture in Steel Cord-Rubber Composites, ***G.E. Hammer***, The Goodyear Tire & Rubber Company

In steel cord-rubber adhesion testing high rubber coverage, or cohesive fracture in the rubber, is generally accepted as a necessary condition for good adhesive bonding. On the microscopic level the transition from high rubber coverage to exposed wire is a transition from fracture in the rubber to separation in the sulfide layer in the adhesive interphase. This sulfide layer is a mixture of copper(I)- and zinc sulfides. Multivariate statistical analysis of Auger depth profiles of the interphase produced chemical depth profiles from which the composition of the interfacial sulfide (percent zinc sulfide and copper(I)sulfide) can be measured. For a variety of compounds, cures, and aging conditions the rubber coverage was a function of the percent zinc sulfide, with rubber coverage dropping abruptly as the percent zinc sulfide increased from 60 to 80%; specifically the a rubber coverage of one-half the initial value appeared to correspond to a percent zinc sulfide of 75%. A mechanism has been proposed wherein the loss of adhesion was attributed to the one or both of (i) overgrowth of the bonding copper sulfide by the non-bonding zinc sulfide in the interphase, (ii) embrittlement of the sulfide by increased content of zinc sulfide.

AS-ThP5 Electronic States of Fe Atomic Chains on Pt (997) Surface, ***R. Cheng***, *E. Ayieta,* Indiana University-Purdue University, *Y. Losovyi*, Louisiana State University

The study of low dimensional systems is of great interests due to their technical applications as well as the rich fundamental physics. The variety of one dimensional atomic chains can be synthesized on stepped surfaces, which provide opportunities for systematically tailoring the surface properties. The electronic structure of the high vicinal surface plays an essential role to determine the physical properties of the atomic chains as well as the surface catalysis. We have used several surface analysis techniques to study the surface of the (997) single crystal. The scanning tunneling microscopy and low energy electron diffraction results show that the surface has uniform step terrace without any reconstruction. The angle resolved ultra violet photoemission spectroscopy was performed to characterize the band structure of Pt(997) surface by using synchrotron radiation source. Then Fe were carefully deposited on to Pt(997) substrate at room temperature. The atomic resolution STM data shows that Fe atomic chains were formed along the step edges due to the step decoration. Finally angle resolved ultra violet photoemission spectroscopy was also performed to characterize the Fe atomic chains.

AS-ThP6 Using a Dual-Beam SIMS to Study Nano-scale Metallic Thin Films and Biological Samples, ***H. Chen***, *T. Bunai, E.R. Tracy, W.E. Cooke, A.L. Wilkerson,* College of William and Mary, *S. Rossnagel,* IBM T.J. Watson Research Center, *D. Manos*, College of William and Mary

Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) offers high sensitivity and mass resolution. It is used widely in both research laboratories and industry. While TOF-SIMS is a well established surface analyzing method, high resolution depth-profile analysis is often desired in semiconductor industry, nano-structure manufacturing and engineering. Using a TRIFT II dual-gun system, which is equipped with a Au_n^+ gun as primary beam and an Argon gun as sputter beam, we studied a series of samples that consist of multilayer, nano-scale metallic thin films. Depth profiling is carried at different sputter energies (500eV-5keV) and the resolution is compared for these different sputter energies. Using the imaging capability of TOF-SIMS, the image of the crater after sputtering is obtained and the ion mixing at interface is studied. The result is compared with TRIM simulations. One great advantage that TOF-SIMS offers over other types of mass spectroscopy like MALDI is sub-micron spatial resolution. MALDI is the primary method used in mass spectroscopic imaging of biological samples like cells and tissue sections. Though MALDI offers a wide mass range, the spatial resolution, limited by the matrix crystal size and laser beam spot size, is often tens of microns. SIMS high spatial image is a well suited complement to MALDI image. The argon sputtering, though primarily used to study inorganic samples, was recently used to expose cell inner structures for electron microscopy images. Using the dual-beam system, we studied a prostate tissue section. The sputtering rate is determined, and depth-profiles are correlated to interior cell structures in the SIMS image.

AS-ThP7 Characterization of Mobile Ions in Insulating Materials and Their Effect on Polymer Adhesion, ***K.M. Stika***, DuPont, *K. Proost, A. De Backer,* DuPont-Belgium, *J.R. Marsh, D.E. Davidson, D.G. Swartzfager, K.G. Lloyd*, DuPont

Adhesion of polymers to inorganic substrates can be seriously affected by the surface and interfacial chemistry of the adjoining layers. Modification of the substrate through heating, chemical treatment, accelerated aging or environmental exposure has been shown to contribute to the ultimate adhesion performance of laminate and multilayer structures. Similarly, diffusion of ions from a glass surface with the formation of a leached ion layer under varied conditions is also a well known phenomenon. It follows that the ability to control and profile elemental composition and depth distribution of highly mobile ions in the near surface region of inorganic materials is an important tool for the fundamental understanding of polymer/inorganic adhesion. This presentation will highlight recent efforts to profile near surface mobile ions as a function of substrate aging or surface treatment and the correlation of these chemical profiles with changes in polymer/inorganic adhesion performance.

AS-ThP8 Molecular Dynamics Simulations of 30 keV and 2 keV Ga in Si, ***L.A. Giannuzzi***, FEI Company, *B.J. Garrison*, The Pennsylvania State University

Molecular dynamics simulations of 2 keV and 30 keV Ga bombardment of Si(011) at a grazing angle of 88 degrees show that the dynamics effectively follow scattering from a flat surface and that very little energy is transferred to the substrate. The inclusion of an adatom above the surface allows for the coupling of the energy of motion parallel to the surface into the substrate. The adatom and one other Si atom eject and motion in the substrate occurs down to a depth of 13 Å. These results show that some surface roughness is necessary for sputtering to occur at very grazing angles of incidence (i.e., high incident angles). Therefore, it is unlikely that focused ion beam polishing can create a non-facetted or atomically smooth surface.

AS-ThP9 Residual Stress of Focused Ion Beam-Exposed Polycrystalline Silicon, ***K. Archuleta***, University of New Mexico, Sandia National Labs, *D.P. Adams*, *M.J. Vasile*, Sandia National Labs, *J.E. Fulghum*, University of New Mexico

Focused ion beam systems are increasingly utilized to fabricate tools, instruments, sensors and devices on the micrometer and nanometer scales. It is thus critical to understand the impact of FIB bombardment on the relevant properties of different materials. Despite many investigations of implanted gallium concentrations, surface roughening and microstructural changes, few studies have quantified the residual stress that results from FIB exposure. Medium energy (30 keV) focused gallium ion beam exposure of silicon results in a compressive inplane stress with a magnitude as large as 0.4 GPa. Experiments involve uniform irradiation of thin polysilicon microcantilevers (200 µm in length) over a range of dose from 1×10^{16} to 2×10^{18} ions/cm^2. The radii of curvature of microcantilevers are measured using white light interferometry in atmosphere before and after ion beam exposure. The residual stress is determined from these radii and other measured properties using Stoney's Equation. The large residual stress is attributed to ion beam damage, microstructural changes and implantation.

AS-ThP10 Nanoindentation Study of Silicon-on-Insulator (SOI) and Strained (sSOI) Multilayers Composite Films, ***J.E. Jakes***, University of Wisconsin-Madison and USDA Forest Products Laboratory, *D.S. Stone*, University of Wisconsin-Madison, *K. Tapily*, *H. Baumgart*, Old Dominion University, *G. Celler*, SOITEC, Bernier-Grenoble, France, *A.A. Elmustafa*, Old Dominion University

Silicon-on-Insulator (SOI) technology provides an engineered composite substrate where the active top Si device layer is decoupled from the mechanical support wafer by an interspersed electrically insulating and mechanically compliant silicon oxide layer. The main application of SOI technology is found in microelectronics, where SOI offers CMOS performance enhancement with the use of an embedded oxide layer to isolate transistors from the substrate, which results in lower parasitic capacitance and reduced junction leakage and a host of other benefits. For further performance gain lattice strain can be incorporated into SOI films in order to enhance carrier mobility for MOSFETs. Bi-axially tensile strained sSOI films were obtained with a fabrication sequence of epitaxially growing 150 Å to 600 Å strained Si films on a relaxed 20% Ge containing $Si_{1-x}Ge_x$ buffer layer on a donor wafer. During epitaxy the Si lattice stretches to match the larger $Si_{1-x}Ge_x$ lattice. The larger lattice constant of Ge produces a 4.1% lattice mismatch with the Si crystal. The higher the Ge alloy concentration, the higher the embedded strain becomes. Following successful bonding of both wafers, the donor wafer was split off with the Smart Cut^{TM} exfoliation technique. The surface was then finished with an etching process to completely remove all traces of the $Si_{1-x}Ge_x$ film, resulting in a Ge-free bi-axially strained Si film on amorphous SiO_2 insulator. In this work we use nanoindentation to investigate the hardness and modulus of standard relaxed SOI and bi-axially tensile strained sSOI with Si films ranging in thickness from 10 to 60 nm and extreme strained xsSOI multilayer samples. The elastic response of the silicon-oxide-silicon substrate multilayer system to indentation can be modeled using elasticity theory, which reveals excellent agreement with the experimental results. The nanoindentation experiments detect a 5% difference in composite modulus with indent depths between 30 and 40 nm deep for 60 nm-thick tensile strained sSOI films compared to SOI films. These strained films are grown epitaxially on a $Si_{0.80}Ge_{0.20}$ buffer layer followed by wafer bonding and film exfoliation by the Smart Cut^{TM} technology. The sSOI and xsSOI thin films exhibit mean tensile stress levels of 1.3 GPa and 2.5 GPa respectively using a $Si_{0.60}Ge_{0.40}$ buffer layer.

AS-ThP11 Study of Photocatalytic Activity in the Low Temperature-Annealed TiO_2 Thin Film Prepared by Sol-Gel Technique, ***A. Majumder***, *S. Biswas*, *M.F. Hossain*, *T. Takahashi*, University of Toyama, Japan, *Y. Kubota*, University of Yokohama City, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

Semiconductor photocatalysts, particularly titanium oxide (TiO_2) with high photocatalytic activity, offers convenient route of purification of air and water and a provision of 'self-maintaining' clean surface. Several physical and chemical techniques have been used to prepare titanium dioxide thin film. Among the various techniques, the relatively simple sol-gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. However, generally post-deposition annealing at high temperature is required for achieving crystalline phase. Crystallinity is one of the key factors behind the photocatalytic activity of TiO_2, therefore achievement of better crystallinity at relatively low temperature is an important issue. In our present study, the titanium dioxide porous films were deposited on glass slides by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane was hydrolysed in a water/alcohol/acetic acid mixture. The solution thus prepared was deposited on glass substrates. These films were transparent and crack free. All the films were annealed at different annealing temperatures, ranging from 350° C to 500°C. Sufficiently good crystalline sample was obtained by annealing at 350° C. For this present investigation; annealing temperature and number of coating layers were varied. The sol was initially characterized by DTA-TGA. The structure and optical characterizations of these films were made by X-ray diffraction and UV-Vis spectroscopy, respectively. XRD patterns of all the titanium dioxide films confirmed the anatase structure. The surface morphology of the films was observed by atomic force microscope (AFM) and scanning electron microscope (SEM). The morphology of porous titanium dioxide thin films strongly depends on annealing temperatures and number of coatings. The photocatalytic activity of the TiO_2 thin films was evaluated by the decomposition of methanol with the help of FTIR spectroscopy. It has been observed that the photocatalytic activity of the TiO_2 thin films increases with the optimization of annealing temperature as well as with the increase of the numbers of layers. The variation of photocatalytic activity with different annealing temperatures and different number of layers is interpreted in terms of different crystallinity, porosity and surface morphology.

Authors Index

Bold page numbers indicate the presenter