Monday Afternoon, October 18, 2010

Marine Biofouling Topical Conference
Room: Navajo - Session MB+BI+AS-MoA

Preventing & Characterizing Marine Biofouling
Moderator: G.P. Lopez, Duke University

2:00pm MB+BI+AS-MoA1 Zwitterionic Polymers for Non-Fouling Coatings, *G. Tew*, University of Massachusetts Amherst **INVITED**
Biofouling remains a challenging problem for various fields ranging from biomedical applications and marine coatings technology, to water purification, transport, and storage systems. To date, the most widely employed protein repellent materials are poly(ethylene glycol) (PEG) or oligo(ethylene glycol) (OEG) based. Even though PEG shows excellent nonfouling character, it has low stability in the presence of oxygen and transition metal ions found in most biochemical solutions, which pushed the field to search for more robust non-fouling materials. Having hygroscopic nature similar to PEG as well as a biomimetic character, arising from their structural similarity to the head groups of lipids comprising cell membranes, zwitterions such as 2-methacryloyloxyethyl phosphorylcholine (MPC) and more recently carboxy/sulfobetaines have also been investigated as protein resistant materials. These materials concentrate only on hydrophilic modification of the substrates. However, the real biological environment is populated by different species, which have different attachment mechanisms; some prefer to adhere more on hydrophilic surfaces whereas others prefer more hydrophobic substrates. The solution to this problem has been investigated by engineering surfaces that reconstruct depending on the environment they are being exposed to, which has been found to be relatively easy to obtain with amphiphilic materials. However, these approaches are either still not sufficient to inhibit bioadhesion by themselves or they suffer from complex or labor intensive coatings preparation conditions. In this work, we are introducing a new polymeric system which carries dual functionality at the repeat unit level, a zwitterionic functionality coupled with an alkyl moiety that can be varied to adjust the amphiphilicity of the overall system. The alkyl group is varied to include PEG based, hydrocarbon, and fluorinated chains. Using these ring-opening metathesis polymerization (ROMP) based zwitterionic polymers as the foundation for non-fouling coatings, we are trying to understand what role the overall hydrophilicity/amphiphilicity of the materials play in fouling prevention.

2:40pm MB+BI+AS-MoA3 Resistance of Saccharide-Terminated Alkylthiol Self-Assembled Monolayers to Protein Adsorption and Marine Biofouling, *T. Ederth*, T. Fyrner, T. Ekblad, M. Hederos, H.-H. Lee, A. Mangone, P. Konradsson, C.-X. Du, Linköping University, Sweden, *M.E. Pettitt, M.E. Callow, J.A. Callow,* University of Birmingham, UK, *S.L. Conlan, A.S. Clare,* University of Newcastle, UK, *F. D'Souza, G.T. Donnelly, A. Bruin, P.R. Willemsen,* TNO Science and Industry, The Netherlands, *B.G. Liedberg*, Linköping University, Sweden
The protein resistance of galactoside-terminated alkanethiol self-assembled monolayers (SAMs) can be tuned by partial methylation of the terminating saccharides, and has a non-trivial dependence on the degree of methylation [1], and for other mono- and oligosaccharide-terminated SAMs, protein resistance may vary considerably with small changes in sugar structure. We have used such mono- and oligosaccharide-terminated SAMs in a series of assays using marine fouling organisms as biological model systems, representing common micro- and macrofoulers. We investigate to what extent protein resistance properties are related to effective prevention of fouling by the marine model organisms, and discuss the results in terms of physicochemical properties of the SAMs.

[1] Hederos, M.; Konradsson, P.; Liedberg, B., *Langmuir* **2005,** 21(7), 2971-2980. DOI: 10.1021/la047203b

3:00pm MB+BI+AS-MoA4 Influence of the Characteristics of a Mineral Coating on its Ability to Resist to the Biofouling, *T.H. Tran*, Ecole Nationale Supérieure des Mines de Saint Etienne, France
Mortars are building material with a high primary bioreceptivity and thus, they are easily colonized by different microorganisms... But green algae and cyanobacteria are the main which affect the aesthetics of the facade. Besides the aesthetical problem, an economical problem exists because of the expensive restoration of facade.

This work aimed to study the influence of the intrinsic parameters of a Portland cementitious mortar (roughness, porosity and surface alkalinity) on the algae development in laboratory and also in situ experiments. The degree of fouling was evaluated by means of colorimetric measurements and image analysis.

The roughness played an important role in algae establishment: the higher the roughness, the easier the algae adhesion. The carbonation, reducing surface alkalinity, shortened remarkably the latency time of the fouling onset.

From experimental results, a model was built to predict the fouling of mortar. This model was based on processes such as "germination" - growth. Each rate law was determined separately by image analysis.

3:40pm MB+BI+AS-MoA6 Influence of Physicochemical Surface Properties on the Settlement of Biofouling Microorganisms, *A. Rosenhahn*, Karlsruhe Institute of Technology, Germany **INVITED**
When manmade surfaces are immersed into the ocean, biofouling rapidly occurs. To support the outphase of toxic coating formulations from the market we derive design rules for environmental benign alternatives. Therefore we study the interaction of biofouling organisms such as zoospores of the green seaweed Ulva linza with well defined surfaces and disentangle the influence of wetting, hydration, morphology, and charge. The obtained results are discussed in the context of time depending formation of conditioning layers. Especially because of its motility, the settlement step of Ulva is highly selective and crucial in their life cycle. A detailed investigation of the relevant phases of approach, exploration and eventually settlement is desired but challenging due to the quick, three dimensional swimming motions of spores. Digital in-line holography is suited for this application as time lapse holograms recorded with a single detector provide the 3D position of microorganisms with high accuracy and at a high frame rate. From such 4D tracking data, the sensitive response of spores and their interaction with surfaces has been studied. Statistical analysis of the motion pattern occurrence, velocity distributions and turning motions on surfaces with different chemical termination can be correlated with the accumulated biomass. By this we obtain quantitative access to the interaction between single spores and surfaces.

4:20pm MB+BI+AS-MoA8 Interfacial Spectroscopy: *In situ* **Approaches to Understand Sticky Contacts**, *K.J. Wahl*, D.E. Barlow, R.K. Everett, C.M. Spillmann, Naval Research Laboratory, *G.H. Dickinson, B. Orihuela, D. Rittschof*, Duke University Marine Laboratory **INVITED**
Proteinaceous secretions are widely recognized to be significant contributors to marine biofouling. The resulting interfacial films can be physisorbed or chemisorbed, and have varying degrees of permanency – they may be highly polymerized and cross-linked, or simply sticky enough to allow surface exploration. Conventional approaches to examining interfacial films derived from bioadhesive junctions is forensic in nature – foulant removal (separating the surfaces) followed by *ex situ* examination of the adhesive composition and surface morphology. While "what" the adhesive is may be gleaned from *ex situ* approaches, "how" the adhesive is applied and cures cannot. These time dependent changes can't be examined "after the fact" and instead require real-time measures of interfacial interactions.

At NRL, we have made significant progress in developing *in situ* methods to demonstrate the chemical, mechanical and rheological processes in interfaces. We are now applying and extending these approaches to examine underwater adhesion in marine organisms, specifically the little striped barnacle, *Balanus amphitrite*. We are developing *in situ* and *in vivo* spectroscopic approaches to determine how protein structure and chemistry influence marine foulant adhesion. We are particularly interested in determining the structure and chemistry of the cement, the biochemical processes influencing polymerization, cross-linking, and water displacement, as well as the physiochemical nature of the adhesion. Our *in situ* approaches include performing temporally- and spatially-resolved microscopy and spectroscopy through adhesive interfaces transparent at UV, visible, IR, and x-ray wavelengths. I will describe how we have used these tools to develop new understanding of the properties and development of the adhesive interface of barnacles.

5:00pm MB+BI+AS-MoA10 Solid State Circular Dichroism of Insoluble Bioadhesive Films: Determining Protein Secondary Structure by Concentration Independent Analysis, *D.E. Barlow*, *J.L. Kulp, K.J. Wahl*, U.S. Naval Research Laboratory
Far-UV circular dichroism (CD) is a valuable method for estimating protein structure components. Analysis of protein CD spectra typically requires

deconvolution to resolve overlapping bands and standard methods require that the concentration and pathlength of the sample are accurately known. While this is usually not an issue for the solution state, it is sometimes desirable or a necessity to analyze samples as solid films, complicating deconvolution. Barnacle cement is one example of a proteinaceous bioadhesive that is insoluble by standard biochemical methods and of inconsistent thickness in the native state. To analyze such samples by CD, we have applied g-factor analysis,[1] where the CD spectra are normalized by absorption spectra. This has been demonstrated as a valid, concentration independent deconvolution method, but so far has not been widely used. We will present protein secondary structure estimation results of barnacle cement films as determined by g-factor analysis and show how these results compare with those obtained by infrared spectroscopy. Potential issues and further applicability of solid state CD for bioadhesion studies will be discussed.

[1] McPhie, P. *Anal. Biochem.* **2001**, *293*, 109.

5:20pm MB+BI+AS-MoA11 Dissipative Microbalance (QCM-D) Studies of Interfacial Processes at the Nanoscale, *M.A. Poggi*, Biolin Scientific

Currently there are many technologies that can study the bulk properties of nanoparticles in solution (such as light scattering) as well as experimental methods that allow one to visualize particles (microscopy or fluorescence). However, there are few technologies that can provide real-time in-situ information regarding how nanoparticles interact with other molecules or materials. Recently we have been using the quartz crystal microbalance with dissipation monitoring technology (QCM-D) to quantify the interaction of particles with surfaces and other materials (biological and organic). We will first present recently published results that address the effect of stagnant and dynamic motion of chemically modified nanoparticles on their adsorption onto silica surfaces. We were able to follow the real-time assembly (in liquid) of these chemically-modified particles. By simultaneously quantifying the changes in surface mass and viscoelasticity during the adsorption process, we were subsequently able to model the adsorption characteristics of these nanoparticles. We will also discuss recent advances that have been made in regards to using QCM-D to follow the assembly of biological nanoparticles (such as cells, viruses and lipids) and polyelectrolytes and touch upon recent electrochemical work that we have been using to study electroactive processes at interfaces.

Tuesday Morning, October 19, 2010

Applied Surface Science
Room: Cochiti - Session AS-TuM

Electron Spectroscopies
Moderator: S.R. Bryan, Physical Electronics

8:00am **AS-TuM1 Recent Developments in Quantitative XPS and AES**, *C.J. Powell*, National Institute of Standards and Technology
INVITED
An overview will be given of some recent developments to improve quantitative XPS and AES [1]. First, guidance is now available for choosing integration limits in the measurement of XPS peak intensities [2]. A recent comparison of reported peak intensities in simulated XPS spectra with known intensities showed large deviations if the integration limits were chosen inappropriately. Second, Tanuma et al. have reported a new set of inelastic mean free paths (IMFPs) for 41 elemental solids that were calculated from experimental optical data for electron energies from 50 eV to 30 keV [3]. These IMFPs agree well with recent calculations and measurements. Third, examples will be given of the use of simple predictive formulae that are available for the effective attenuation length, mean escape depth, and information depth in AES and XPS [4]. Fourth, the effects of elastic scattering and analyzer-acceptance angle on the analysis of angle-resolved XPS data have recently been analyzed [5]. Calculations were made of photoelectron intensities at selected emission angles for films of $SiO_{1.6}N_{0.4}$ and $HfO_{1.9}N_{0.1}$ of various thicknesses on Si with the NIST SESSA Database [6]. Ratios of intensities for each line from the film for the least realistic model condition (elastic scattering "off", small analyzer-acceptance angle) to those from the most realistic model condition (elastic scattering "on", finite analyzer-acceptance angle) changed relatively slowly with emission angle but the corresponding intensity ratios for the Si(substrate) 2p line changed appreciably with emission angle; such changes can lead to erroneous results in the analysis of angle-resolved XPS data [5]. Fifth, examples will be given of a new NIST database to provide backscattering correction factors for AES using an advanced model that accounts for attenuation of the primary beam in the surface region of the sample and the instrumental configuration [7]. Finally, mention will be made of a set of reference energies for 59 Auger transitions in 42 elemental solids that should be useful for the determination of chemical shifts in AES and XPS [8].

[1] C. J. Powell and A. Jablonski, J. Electron Spectrosc. Relat. Phenom. 178-179, 331 (2010).

[2] C. J. Powell and J. M. Conny, Surf. Interface Anal. 41, 804 (2009).

[3] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. (to be published).

[4] A. Jablonski and C. J. Powell, J. Vac. Sci. Technol. A 27, 253 (2009).

[5] C. J. Powell, W. S. M. Werner, and W. Smekal (to be published).

[6] http://www.nist.gov/srd/nist100.htm .

[7] A. Jablonski and C. J. Powell (to be published).

[8] C. J. Powell, J. Electron Spectrosc. Relat. Phenom. (to be published).

8:40am **AS-TuM3 Effect of Monochromator X-ray Bragg Reflection on Photoelectric Cross Section**, *A. Herrera-Gomez*, CINVESTAV, Mexico

9:00am **AS-TuM4 Photovoltage, Photoconductivity and Charging Probed by Dynamical XPS Measurements**, *S. Suzer*, Bilkent University, Turkey
We have developed a technique for recording the shifts in the positions of the XPS peaks in response to different forms of electrical stimuli for probing dynamics of charging/discharging processes of thin dielectric films, which we have named as Dynamic XPS. Modulation of the electrical signals in the forms of square, sinusoidal and triangular waves at different frequencies enables us to extract some dielectric properties of surface structures, such as effective resistance, and capacitance values in a chemically resolved fashion. We have also introduced photo-illumination as an additional form of the stimuli and have been using this technique for investigating the combined optical + electrical responses of semiconductive (Si and GaAs) as well as photoactive (CdS and TiO_2) materials towards better understanding of the different photo-processes, like photoconductivity and/or photovoltage development, etc. We use our dynamic measurements to help in distinguishing various fundamental processes, by using the frequency dependence as an additional tool. This makes XPS a more powerful technique for characterizing today's demanded

nano or optoelectronic devices. The methodology will be introduced, and several examples will be presented.

9:20am **AS-TuM5 Order-Disorder Transition for Corrugated Au Layers**, *K. Fukutani*, University of Nebraska-Lincoln, *N. Lozova*, Louisiana State University, *S.M. Zuber*, University of Wroclaw, Poland, *N. Wu, P.A. Dowben*, University of Nebraska - Lincoln, *P. Galiy*, Ivan Franko National University of Lviv, Ukraine, *Y.B. Losovyj*, Louisiana State University
Atomic-scale structure of the growth of a gold film on Mo (112) was investigated by means of low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) up to several monolayers (ML) of gold coverage. Both LEED and STM results establish that Au grows on Mo(112) in a layer-by-layer mode, for at least the first two monolayers. A number of ordered structures are formed and both the first and second layers adopt the Mo(112) 1x1 surface structure upon completion. For some gold layers on Mo(112), notably the 1.66 monolayer 3x1 and 1.75 monolayer 4x1 gold overlayers, we find evidence of a phase transition associated with increasing disorder in gold layers with structural corrugation and anisotropic band structure. The signature of this phase transition, at temperatures in the range of 400–500 K, is a sharp decrease in the overlayer effective Debye temperature. Angle-resolved photoemission spectroscopy (ARPES) suggests coverage dependent changes in the electron-phonon coupling for gold adlayer.

9:40am **AS-TuM6 Surface Characterization of Gold Nanoparticles and Their Interaction with Protein G B1 Domain**, *S. Techane, L. Baugh, L.J. Gamble, P.S. Stayton*, University of Washington, *D.R. Baer*, Pacific Northwest National Laboratory, *D.G. Castner*, University of Washington
The purpose of this research is to study the interactions of biomolecules with nanoparticles using model systems. Model proteins and nanoparticle surfaces are used to simplify the complex biological/nanoparticle surface environment and develop a fundamental understanding of the interactions at this interface. Protein G B1 domain was used as a model protein. Wild type Protein G B1 (WT) has a uniform distribution of negatively charged residues on its surface. Using site-directed mutagenesis to neutralize six charged residues at one end of the protein, a mutant (Δ6) was created possessing a global charge dipole along its long axis. This variation in surface charge affected the biomolecular interaction with nanoparticle surfaces. Gold nanoparticles (AuNPs) with self-assembled monolayers of carboxylic alkanethiols (COOH-SAM) were used as the well-defined model surface.

We previously reported that AuNPs 14nm in diameter and functionalized with C16 COOH-SAM were more monodisperse in size and shape relative to those with larger diameter, and more stable in solution relative to those functionalized with shorter-chain COOH-SAMs. To accurately interpret XPS data and account for the curvature effect, and to quantitatively analyze overlayer thickness (T) and roughness (R), we used SESSA combined with geometric correction methods. The C16 COOH-SAM on flat Au was modeled with SESSA at photoelectron take-off angles from 5 to 85˚. Corresponding ARXPS experiments were also performed. T and R were optimized to find the best agreement between the simulated and experimental results. It was necessary to add a hydrocarbon contamination layer (CL) at the surface of the COOH-SAMs in the simulations. For the C16 COOH-SAM on flat Au, the best conditions were $T=1.1Å/CH_2$, R=1.05 and CL=1.5Å. After applying a geometric correction, $T=0.9Å/CH_2$ and R=1.05 was obtained for the SAM on AuNPs with similar CL. Studies to minimize CL are underway.

WT and Δ6 B1-protein G were adsorbed onto 14nm-AuNP-C16 COOH-SAM at various protein concentrations. Following adsorption and centrifugation, the final supernatant containing unbound protein and AuNPs with bound protein were analyzed by colorimetric assay and XPS, respectively. Both methods showed that Δ6 adsorbed more than WT. As Δ6 concentration increased, the N signal (unique to the protein) increased and the Au signal (unique to the surface) decreased, following similar trends as observed in the adsorption isotherm curve. Based on our preliminary study, a %N of 13.6 ± 0.3 corresponded to a monolayer of ~$0.95\mu g/cm^2$. Further studies to accurately determine thermodynamic adsorption parameters and the AuNP concentration are underway.

11:00am **AS-TuM10 Charging Compensation Method in XPS with Positive Voltage and Low Energy Electron Beam**, *M. Shima, K. Tsutsumi, T. Tazawa*, JEOL Ltd., Japan
X-ray photoelectron spectroscopy (XPS) is widely used for qualitative, quantitative and chemical state analysis on various material surfaces, because XPS can obtain more stable spectra even in charged insulator

surfaces than Auger electron spectroscopy. However in many cases, XPS spectra would be even distorted and shifted to high binding energy side by the positive surface charging caused by photoelectron emission. And we identify the chemical state of materials from peak position and peak shape. As a result, such a charging effect reduces the usefulness of XPS. The most widely used method for suppression of surface positive charging is to irradiate low energy electron to the sample surface. But operator should select electron flood gun conditions carefully such as accelerating voltage and the amount of the electron flux, because once the electron flux and accelerating voltage is set too high, peak shape will be distorted again and peak position turn to the lower binding energy side.

At this time, we propose a new charge compensation method that electrons irradiated from flood gun will be maintained efficiently on an insulator surface by applying positive voltage underside of insulator sample. The mechanism of this method is to accumulate excess electrons on the top of an insulator like a capacitor. Electrons maintained on insulator sample surface remove the differential positive charging, even when X-ray irradiation makes another differential charging. In addition, our experiment results shows that surface potential of insulator sample is determined simply by accelerating voltage of flood gun and it is independent of applied positive voltage for sample under the conditions that adequate electrons are supplied from flood gun. It is found that this charge compensation method has ideal mechanism; we can control not only peak shape in ideal shape but also its peak position.

In the presentation we will show some XPS experimental results with this method and discuss them.

11:20am **AS-TuM11 Applications of Hard X-ray Photoelectron Spectroscopy for Characterization of a Hybrid Ti-Si Sol-Gel**, *J.L. Fenton, G. Mitchell, Y. Srivastava, Y.Q. Rao, B. Weaver, R. Auger*, The Dow Chemical Company
Hard x-ray photoelectron spectroscopy (HAXPS), in particular variable kinetic energy photoelectron spectroscopy (VKE-XPS), is becoming increasingly useful to determine chemical and elemental information from the "bulk" of materials compared to traditional XPS. In addition, VKE-XPS allows for non-destructive depth profiling of materials that pose a greater challenge for Angle-Resolved XPS (ARXPS) such as materials with rough surfaces. This talk will present the application of VKE-XPS to hybrid Ti-Si based sol-gels to understand potential chemical or elemental changes as a function of excitation kinetic energy.

11:40am **AS-TuM12 Inline Production Monitoring of Carbon Doped Polysilicon Using X-Ray Photoelectron Spectroscopy**, *B. Dickson*, ReVera Incorporated, *H. Lee, W. Namkoong,* Samsung Electronics Co., *M. Kwan, H. Pois, T.C. Larson*, ReVera Incorporated
X-ray photoelectron spectroscopy [XPS] is a well respected compositional and thickness metrology technique. Historically, XPS has been used as an off-line characterization method limited to laboratories. The introduction of fully automated, small spot XPS systems in the fab now enables in-line metrology with results in minutes instead of days. This paper details the production control monitoring of carbon composition in carbon doped polysilicon films which are used in flash devices. Measuring carbon doped polysilicon for inline production has two main challenges: sensitivity and stability. Sensitivity to different carbon dosage processes as well as the process variation of day to day production has been demonstrated. In addition to compositional sensitivity, high resolution XPS can measure the different chemical bonding states of C. Because the carbon doped polysilicon surface is very unstable, with surface carbon accumulating on the wafers' surface over time in the form of amorphous carbon and an atomic molecular contamination [AMC] layer, the main carbon dopant bonding state signal is separated from non-doped carbon bonding state signals. For stability, the ReVera Veraflex has developed an application to separate the naturally increasing AMC carbon from the stable doped carbon atomic composition, enabling a robust statistical process control [SPC] method.

Tuesday Afternoon, October 19, 2010

Applied Surface Science
Room: Cochiti - Session AS-TuA

Advances in Surface and Interface Imaging
Moderator: A.V. Walker, University of Texas at Dallas

2:20pm AS-TuA2 Advanced Chemical State Analysis Method with Standard Spectra Measured with a Higher Energy Resolution of 0.1 % in Auger Electron Spectroscopy, *K. Tsutsumi*, **M. Shima**, *A. Tanaka, T. Tazawa*, JEOL Ltd., Japan

Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) are very famous for elemental and chemical state analysis at a solid surface. In generally, XPS has been utilized for these analysis in an area of more than a few 100 mm^2 on a solid surface. In contrast, AES has been used rarely for chemical state analysis, but for elemental analysis at a minute area of less than 100 mm^2. The reason for it is approximately caused by the following three problems.

It is difficult to detect any peak shifts between chemical state differences because almost peaks in an AES spectrum are broader than XPS.

It is difficult to measure stably a standard AES spectrum for an insulator sample because a focused electron beam irradiation causes stronger surface charging.

A focused electron beam often makes some elements change to another chemical state.

Among these problems, No.2 and No.3 can be solved in many cases by some special pre-sampling and measurement techniques. However No.1 has been recognized as the biggest problem for the chemical state analysis in AES because some commercial Auger instruments could not obtain sharper peaks in a spectrum with a poor energy resolution of 0.5-0.6 % or the others could not have a sufficient sensitivity with an energy resolution of higher 0.1 %. So, the chemical state analysis in AES has been carried out only for some specific elements showing a bigger chemical shift of more than a few eV.

Now we had measured more than 400 standard spectra by the latest analyzer for pure materials or compounds with the energy resolution of higher than 0.1 %, which included shaper peaks and fine structures with little electron beam damage. Those spectra show that Auger spectra for compounds have different peak shapes and different peak positions.So, it is possible to distinguish them by the peak shape difference, even if some standard spectra of different chemical states have quite similar peak positions each other.

In this report, we can propose an advanced chemical state analysis by higher energy resolution AES, which is a spectrum separation method from a practical spectrum including several chemical states by comparison of peak shape difference. As an example application, this method was applied for the depth profile result of a natural oxide layer on a pure tin oxide plate with an energy resolution of 0.1 %. The result showed that it was clearly consisted of three layers ($SnO_2/SnO/Sn$ subst.) by the waveform separation of Sn MNN to each chemical condition of Sn^{4+}, Sn^{2+}, and Sn^0. Moreover, it was found that the quantitative analysis of chemical state of Sn was also possible by comparison of the absolute intensity of standard spectrum.

2:40pm AS-TuA3 3D Atom Probe Analysis of Embedded Nanoclusters in Oxide Matrix, *S. Kuchihbatla, V. Shutthanandan, B. Arey,* Pacific Northwest National Laboratory, *R. Ulfig, T. Prosa,* Cameca Instruments Inc., *C.M. Wang,* **S. Thevuthasan,** Pacific Northwest National Laboratory, *P. Clifton,* Cameca Instruments Inc.

The influence of embedded nanoclusters on the optical, magnetic and electrical properties of bulk and surface oxides has been an active area of investigation. The establishment of new atom probe tomography (APT) and related high-resolution chemical imaging facilities at EMSL, the Environmental Molecular Sciences Laboratory, provides a world-class user facility for performing nanoscale microscopy. In this study we report on Au-rich nanoclusters that have been embedded into MgO and TiO_2 substrates. The effect of high temperature annealing on the properties of the matrix and the secondary phase (Au) are studied in detail. Electron microscopy analysis has shown that the embedded metal particles are often associated with various defects, which further contribute to property modification.

We report the first Local Electrode Atom Probe (LEAP®) analysis of bulk MgO and TiO_2 implanted with 2 MeV Au ions using the accelerator facility at EMSL. Both as-implanted and annealed samples were critically analyzed using a combination of APT and the results are compared with high-angular annular dark-field scanning transmission electron microscopy (HAADF STEM) imaging. High-resolution transmission electron microscopy (HRTEM) clearly resolves the Au-rich nanoclusters and allows observation of the pronounced vacancy clustering associated with these features [1]. These Au-rich nanoclusters were also observed in the atom probe data with the average cluster size (~ 5 nm diameter) in good agreement with those seen using HRTEM. The APT technique, however, due to the high three-dimensional (3D) spatial resolution, is also able to detect the presence of finer-scale Au clusters. It can also directly measure residual Au composition within the MgO matrix and any MgO-Au mixing within the clusters. Besides variations in compositional microstructure, evolution of mass spectrum quality as a function of Au content is also observed. Efforts are ongoing in EMSL to confirm this observation and eliminate the possibility of any contribution from experimental artifacts.

During the course of this presentation we will highlight the advantages of using 3D APT in combination with electron microscopy. Specifically, correlative microscopy provides a means to evaluate the capability of APT to detect the presence of the vacancy clusters.

[1] Wang et al., Applied Physics Letters **87**, 153104, 2005

3:00pm AS-TuA4 Novel Nanoscopic Light Source for Tip‑Enhanced Raman Spectroscopy, *Y.-T. Li*, University of Cambridge, UK, *D. Roy,* National Physical Laboratory, UK, *M.E. Welland*, University of Cambridge, UK

4:00pm AS-TuA7 Imaging of Coal Speciation Using TOF-SIMS and Scanning Transmission X-Ray Microscopy (STXM), *B.P. Yatzor,* University at Buffalo, *H.D. Liang,* China University of Mining and Technology, China, *J.A. Gardella Jr.*, University at Buffalo

A significant problem in the combustion of coal is the release of toxic elements into the atmosphere in gaseous and solid (particulate) forms. In China, villagers use coal, exposed at the surface by erosion, to heat their homes and cook their meals. It is believed that coal combustion is a potential source of endemic diseases [1, 2].

Coal samples were collected from the province of Guizhou in China. In this study, an ION-TOF V equipped with a bismuth primary ion source was used to analyze coal directly without any chemical treatment. Mechanical polishing was performed to create a flat surface for analysis. Analyses revealed that there are distinctions between the organic and inorganic phases of coal. Fluorine was been determined to come from an inorganic phase rather than an organic phase. Two different forms of elemental sulfur were determined through ion imaging. The first one was determined to be organic in nature, while, the second derives from pyrite (FeS_2).

The high spatial resolution of TOF-SIMS can be used to distinguish between different domains in coal, revealing the relationship between specific components suspected of involvement in toxicity of particulate emissions and the coal components.

STXM images, from powder samples suspended on Si_3N_4 windows, show complementary chemical images of carboxylic, aromatic and carbonate species from the C_{1s} edge. Studies were performed using the third generation Canadian Light Source synchrotron facility located in Saskatoon, Saskatchewan. The soft microscopy beamline (10ID-1) was used for analyses.

Spectral shifts in STXM NEXAFS spectra allow carbonate species to be distinguished from carboxylic species. With the help of reference materials, aromatic species could be distinguished from aliphatic species. However, using TOF-SIMS for distinguishing such species would prove to be very difficult, which is why STXM is a good complementary technique for coal studies.

[1] Finkelman *et al.* (2004) *Int. J Coal Geol.* **59**, 19–24.

[2] Finkelman *et al.* (2002) *Int. J Coal Geol.* **50**, 425– 443.

4:20pm AS-TuA8 From Depth Profiling to FIB Sectioning for 3D TOF-SIMS Imaging of Organics, *G.L. Fisher, S.R. Bryan,* Physical Electronics, *P. Lu,* General Motors Company, *N. Smith,* Oregon Physics, *C. Szakal*, NIST

TOF-SIMS characterization of materials in the range of several microns from the sample surface has become somewhat routine. Nevertheless, there are practical limitations to the use of ion beam sputtering for probing both organic and inorganic specimens beyond the surface region. Certain matrix components do not sputter well and are susceptible to ion beam-induced molecular damage. This accumulated beam damage gives rise to incorrect molecular distributions. Some matrix components may sputter at a different rate than others which results in a misrepresentation of the elemental and

molecular distributions. Finally, the time requirements to achieve uniform (i.e. representative) depth profile analysis under ideal instrumental conditions can become prohibitive. Even under optimized experimental conditions, the efficacy of sputter depth profiling for 3D TOF-SIMS imaging is limited to < 5 μm in the case of a favorable matrix and to < 300 nm in the case of an unfavorable matrix. An alternative approach for 3D TOF-SIMS imaging the interior of a specimen is to utilize FIB milling and sectioning. With FIB milling, the interior of a specimen is revealed to depths of ~ 50 μm within a reasonable analytical timeframe. Additionally, 3D chemical imaging of ~ 10 μm deep volumes may be achieved in the same time it would take to perform a low voltage sputter depth profile. The advantage of the FIB-TOF approach is that the artifacts caused by sputter depth profiling, i.e. differential sputtering and accumulated ion beam damage to matrix molecules, are avoided. The union of successive FIB sectioning and TOF-SIMS analysis cycles to achieve 3D chemical imaging will be discussed and illustrated using inorganic and organic examples.

4:40pm AS-TuA9 Mapping of a Polymer Surface Reaction: Determination of the Spatially Resolved, Hydrolytic Degradation Kinetics of a Micropatterned Bioresorbable Membrane, *M.D. Marchany, I.T. Ozbolat, B. Koc, J.A. Gardella, Jr.*, SUNY at Buffalo
Poly(L-lactic acid) (PLLA) is a synthetic, bioresorbable polyester that is extensively used and studied for many [FDA-approved] commercial applications – such as therapeutic drug delivery and tissue engineering scaffolds.[1] It is generally accepted that the degradation process of bioresorbable polyesters: a) is diffusion-based,[2] b) occurs in a region of finite thickness, forming an erosion front that moves towards the center of a polymer structure,[2] and c) its rate increases with higher polymer surface area.[3] Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has been previously used to determine initial (before the onset of weight loss) degradation kinetics at bioresorbable polymer surfaces.[4] This analytical method, combined with the high lateral resolution capabilities of imaging with a bismuth ion source, and image processing algorithms, allowed us to determine the spatially-resolved initial degradation kinetics of micropatterned PLLA membranes at several pH levels. The results show that the degradation reaction occurs at different rates, and that these rates depend on the area of the feature. The findings of this study imply that polymer degradation can be controlled not only in a temporal manner, but also in a microspatial manner, by altering micropattern geometry and size distribution across the polymer membrane.

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5:00pm AS-TuA10 Approaches towards Analyzing XPS Multispectral Image Series (Multi-Sample Analysis) and Combining Multiple Spectroscopic, Microscopic and Macroscopic Analytical, *K. Artyushkova*, University of New Mexico
Applications of multivariate analysis (MVA) methods to surface analysis imaging datasets have increased quite significantly in recent years. Multivariate analysis of 3D imaging TOF-SIMS and XPS data is now quite widely applied (even routinely used by some research groups). Data preprocessing, scaling and selection of appropriate multivariate analysis method have been discussed in the literature quite extensively in a couple of recent years.

What has been addressed in a lesser extent is an important problem of combining quantitative analysis of imaging datasets from the same analytical method from various samples (multi-sample 3D imaging) or combining various analytical data (spectroscopic, imaging, or scalar) obtained for the same sample (multi-modal analysis).

Approaches to quantitatively combine imaging datasets from multiple samples will be discussed on example of multispectral XPS imaging data sets acquired from various paper samples.

Multi-modal analysis will be discussed on example of combining spectroscopic (XPS, XANES), microscopic (SEM) and macroscopic (BET surface area and pore size distribution) data from set of non-Pt group metal electrocatalysts for oxygen reduction reaction treated at different temperatures.

5:20pm AS-TuA11 Atomic Scale Structural and Chemical Analysis of Internal Interfaces in Inorganic Materials, *B.P. Gorman, H.L. Guthrey,* Colorado School of Mines*, A.G. Norman, Y. Yan, M. Al-Jassim,* National Renewable Energy Laboratory*, R.P. O'Hayre*, Colorado School of Mines
INVITED
Fundamentally, photovoltaic and fuel cell devices rely upon interfaces for electrical power generation. However, the undesirable formation of poor quality interfaces can also serve to decrease power efficiency. In the case of photovoltaics, interfaces control the generation and extraction of photogenerated charge carriers; however, the formation of dislocations and dopant clustering can result in recombination centers, thus reducing the ability to extract charge carriers. In fuel cells, the three phase boundary between the electrode, gas, and electrolyte controls the cell power output; however, surface contamination at this interface can reduce the electrochemical reaction rate, and thus the power output of the cell. Understanding both of these interfaces at the atomic structural and chemical level allows for a greater understanding of the formation of interface degradation. In order to fully understand the atomic scale chemistry and structure of interfaces in photovoltaics and fuel cells, we have applied a combination of in-situ FIB / SEM electrical probing using EBIC and ex-situ impedance spectroscopy with high resolution analytical STEM imaging and laser pulsed atom probe tomography. These techniques have been applied to III-V based photovoltaics to gain an understanding of dopant profiling across quantum structures and tunnel junctions, and to probe the initial stages of phase separation in multicomponent epilayers. Similarly, EBIC has been used to identify dislocations and grain boundaries in polycrystalline Si photovoltaics, and to determine the atomic level chemistry and structure at these interfaces that leads to an interface acting as a recombination center. Finally, a combination of STEM and atom probe tomography have illustrated 10-17 / cm^3 changes in local Pt, C, and O chemistry and structure around Pt catalysts for use in polymer electrolyte fuel cells. In order to enable atom probe analysis on materials with widely varying field evaporation characteristics, new FIB specimen preparation techniques were required. Details on the complex experimental methods and instrumentation developed in order to enable all of these investigations are illustrated.

Biomaterial Interfaces
Room: Taos A - Session BI2+AS-TuA

Combining Techniques for Biointerface Characterization
Moderator: L.J. Gamble, University of Washington

4:00pm BI2+AS-TuA7 Spatial and Depth Characterisation of Immobilised Biomolecules on Surfaces, *G. Mishra, A.J. Roberts,* Kratos Analytical Ltd., UK*, D.J. Surman,* Kratos Analytical Ltd.*, S.L. McArthur*, Swinburne University of Technology, Australia
Analysis of biomolecules on surfaces is essential to various applications of biosensors and biomolecule engineering. Matrix-assisted laser desorption/ionisation (MALDI) is now a well established technique for mass spectrometry of biomolecules. Different matrix-analyte preparation protocols have been shown to influence the desorption or ablation process resulting in either high or low metastable fragmentation. It has been speculated that following laser ablation the velocities of the analyte and matrix can be regarded as a valuable and meaningful characteristic of the MALDI process. However, the interaction and distribution of the analyte with respect to the matrix is poorly understood. Here we study the distribution of a selection of biomolecules as a function of matrix material using high resolution imaging x-ray photoelectron spectroscopy (XPS). We feel that understanding the depth distribution of biomolecules in the matrix remains factor which would enable us to draw conclusions on the incorporation of the analyte in the matrix. Thus in this study we also investigate the depth distribution using organic depth profiling techniques.

4:20pm BI2+AS-TuA8 Measuring the Orientation of Electrostatically Immobilized Proteins by Time-of-Flight Secondary Ion Mass Spectrometry and Sum Frequency Generation: From a Model Protein G B1 System to Cytochrome, *J.E. Baio, T.M. Weidner, L. Baugh, P.S. Stayton, L.J. Gamble, D.G. Castner*, University of Washington
The ability to orient proteins on surfaces to control exposure of their biologically active sites will benefit a wide range of applications including protein microarrays and biomaterials that present ligands to bind cell receptors. As methods to orient proteins are developed, techniques are required to provide an accurate picture of their orientation. Since no single technique provides a high-resolution image of surface-bound proteins, combinations of surface analytical techniques are required. In this study, we have developed a model system based on the electrostatic immobilization of

a small rigid protein (Protein G B1 domain, 6kDa) to further develop the capabilities of time-of-flight secondary ion mass spectrometry (ToF-SIMS) and sum frequency generation (SFG) spectroscopy as tools to probe the orientation of surface immobilized proteins. A Protein G mutant (D4) exhibiting net positive and negative charges at either end (for pH 6-8) was produced by neutralizing four negatively charged residues closest to the end of the protein (Asp to Asn or Glu to Gln mutations). These mutants were then immobilized onto NH_3^+ and COO^- terminated self assembled monolayers (SAMs) to induce opposite end-on orientations. ToF-SIMS data from the D4 variant on both NH_3^+ and COO^- SAMs showed intensity differences from secondary ions originating from asymmetric amino acids (Asn:70, 87, and 98m/z; Met:62m/z; Tyr:107 and 136m/z at the N-terminus. Leu:86m/z at the C-terminus). For a more quantitative examination of orientation, we developed a ratio comparing the sum of the intensities of ions stemming from residues at either end of the protein. The 50% increase in this ratio, observed between the NH_3^+ and COO^- SAMs, indicated opposite orientations of the D4 variant on the two different surfaces. In addition, SFG spectral peaks characteristic of ordered α-helix (1645cm^{-1}) and β-sheet (1624 and 1675cm^{-1}) elements were observed, with a phase that indicated a predominantly upright orientation for the α-helix, consistent with an end-on protein orientation. We then moved from this model system and extended this analysis to examine the change in orientation of horse heart Cytochrome c on both NH_3^+ and COO^- SAMs. The positively charged region at one end of Cytochrome c binds to the COO^- substrate while the NH_3^+ surface elicits the opposite binding orientation. Again, within the SFG spectra, ordering of the protein α-helices were confirmed by the feature at 1645cm^{-1} and the change in orientation, induced by the two different substrates, is confirmed by intensity differences within ToF-SIMS spectra between ions stemming from asymmetric amino acids (Glu:84 and 102m/z; Asp:72 and 88m/z).

4:40pm BI2+AS-TuA9 NanoBio Imaging for Cardiovascular Researches, *D.W. Moon*, *T.G. Lee, J.Y. Lee, W. Jegal, S.W. Kim*, KRISS, Republic of Korea **INVITED**
NanoScience has been developed to meet the demands on atomic scale characterization and manipulation of materials and devices from semiconductor industries based on the scaling down law. KRISS has been trying to extend the application scope of nanoscience and technology from microelectronics to biomedical areas. Biochemical imaging of cells and tissues is a basic infra-technology in various bio-medical applications. Instead of conventional labeling methodology for bio-molecular imaging with fluorescent dyes, label-free biochemical imaging methodologies for single cells and tissues such as coherent anti-stokes Raman scattering (CARS), secondary ion mass spectrometry (SIMS), and surface plasmon resonance imaging ellipsometer (SPRIE) has been developed and integrated for new biomedical applications, especially for cardiovascular researches.

Preliminary results of nanobio imaging for cardiovascular researches will be reported on the following issues 1) Three-dimensional visualization of atherosclerotic tissue and prompt on-site analysis of chemical profiles by multiplex CARS with intracellular lipids at the single-cell level as well as crystallized cholesterol in necrotic cores. [1] 2) Histological Imaging based on SIMS analysis of myocardial infarction tissues. [2] 3) cell adhesion dynamics of human carotid smooth muscle cells and human umbilical endothelial cells on fibronectin thin films with SPRIE.

Finally, the present status and future challenges 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.

(1) "Multiplex coherent anti-Stokes Raman spectroscopy images intact atheromatous lesions and concomitantly identifies distinct chemical profiles of atherosclerotic lipids", Se-Hwa Kim, Eun-Soo Lee, JaeYong Lee, EunSeong Lee, Bok-Soo Lee, JeongEuy Park ,and DaeWon Moon, Circulation Research, in press (2010)

(2) "ToF-SIMS Analysis of Myocardial Infarcted Tissue", J.-W. Park, M.-J. Cha, H. K. Shon, S.-H. Kim, T. G. Lee, D. W. Moon, and K.-C. Hwang, Surface and Interface Analysis, in press (2010)

5:20pm BI2+AS-TuA11 Determining Antibody Orientation using ToF-SIMS and Fluorescence Imaging of Affinity-generated Patterns, *M. Dubey*, Los Alamos National Laboratory, *F. Liu, H. Takahashi, D.W. Grainger*, University of Utah, *D.G. Castner*, University of Washington
This study assesses the capability of high-resolution surface analytical tools to distinguish immobilized antibody orientations on patterned surfaces designed for antibody affinity capture. High-fidelity, side-by-side co-patterning of protein A (antibody Fc domain affinity reagent) and fluorescein (antibody Fab domain hapten) was achieved photo-lithographically on commercial amine-reactive hydrogel polymer surfaces. This was verified from fluorescence imaging using fluorescently labeled protein A and intrinsic fluorescence from fluorescein. Subsequently, dye-

labeled murine anti-fluorescein antibody (4-4-20), and antibody Fab and Fc fragments were immobilized from solution onto respective protein A- and fluorescein- co-patterned or control surfaces using antibody-ligand affinity interactions. Fluorescence assays support specific immobilization to fluorescein hapten- and protein A-patterned regions through antigen-antibody recognition and natural protein A-Fc domain interactions, respectively. Affinity-based antibody immobilization on the two different co-patterned surfaces generated side-by-side full antibody "heads-up" and "tails-up" oriented surface patterns. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis, sensitive to chemical information from the top 2-3 nm of the surface, provided ion-specific images of these antibody patterned regions, imaging and distinguishing characteristic ions from amino acids enriched in Fab domains for antibodies oriented in "heads-up" regions, and ions from amino acids enriched in Fc domains for antibodies oriented in "tails-up" regions. Principal component analysis (PCA) improved the distinct ToF-SIMS amino acid compositional and ion-specific surface mapping sensitivity for each "heads-up" versus "tails-up" patterned region. Characteristic Fab and Fc fragment immobilized patterns served as controls. This provides first demonstration of pattern-specific, antibody orientation-dependent surface maps based on antibody domain- and structure- specific compositional differences by ToF-SIMS analysis. Since antibody immobilization and orientation are critical to many technologies, orientation characterization using ToF-SIMS could be very useful and convenient for immobilization quality control and understanding methods for improving the performance of antibody-based surface capture assays.

5:40pm BI2+AS-TuA12 Molecular Depth Profiling and 3D Imaging of Biological Samples by ToF-SIMS: From Model Amino Acid Films to Real Biological Cells, *J.P. Brison*, *N. Wehbe*, University of Namur, Belgium, *D.G. Castner*, University of Washington, *L. Houssiau*, University of Namur, Belgium
Time-of-Flight Secondary Ion Mass Spectrometry is now routinely used to obtain molecular information about the surface of complex biological samples and biomaterials. The recent advent of cluster ion beams such as Bi_3^+ and C_{60}^+ provides enhanced sensitivity for high mass fragments, which in turn allows 2D imaging of specific biomolecules with improved sensitivity and sub-micrometer lateral resolution. Molecular depth profiling of biological samples with low chemical damage and high depth resolution (*i.e.*, < 10 nm) has also been shown to be possible by etching with cluster projectiles such as C_{60} and with low energy cesium ions. Since ToF-SIMS also allows the detection of all elements without the need of specific markers, the technique shows great potential for molecular 3D imaging of single cells and could become an inevitable complementary tool to MALDI and fluorescence microscopy for biomedical research in the near future.

However, only few examples of full 3D images of biological cells have been reported in the literature at this time. This limitation probably comes from the facts that preparing the cells for chemical analysis under UHV environment is tedious, and that our understanding of energetic primary ions/biological matter interactions is limited. Fundamental studies of these aspects are indeed difficult during 3D imaging because the cells are complex, heterogeneous, non-flat samples with relatively unknown molecular composition.

In this work, fundamental biological matter/projectile interactions were studied by depth profiling model amino acid films under different ToF-SIMS conditions. The influence of the experimental parameters on the quality of the depth profiles was investigated by measuring the sputter rates, the depth resolutions and the intensities of the molecular ion signals with respect to the chemistry of the target (*e.g.*, arginine vs phenylalanine), the nature of the primary ion species (*e.g.*, C_{60}^+ vs Cs^+) and the bombardment conditions (*e.g.*, fluence and energy). Then the complexity of the model samples was increased by mixing several amino acids and by creating multilayer films. This approach was another step toward the analysis of real biological samples. Again, ToF-SIMS fundamentals were investigated by measuring, *e.g.*, the interface widths between the different organic layers and the signal decay due to the increasing etching fluence. Finally, optimal 3D images of single HeLa cells were acquired and were discussed based on the data obtained for the model amino acid films. The effect of the sample preparation on the quality of the images was also investigated.

Applied Surface Science
Room: Southwest Exhibit Hall - Session AS-TuP

Applied Surface Science Poster Session

AS-TuP1 Application of an Electrospray Technique to Secondary Ion Mass Spectrometry (SIMS), *Y. Fujiwara, N. Saito, H. Nonaka, T. Nakanaga, S. Ichimura*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

An electrospray technique can generate a continuous stream of charged droplets at currents exceeding 1000 nA. We expect that it has a great potential in Secondary Ion Mass Spectrometry (SIMS). Consequently, we investigated beam generation characteristics using the electrospray technique operated at atmospheric pressure and under reduced pressure (i.e., vacuum).

When electrospraying is performed at atmospheric pressure or above, emitted charged droplets and ions are required to be sampled through an aperture into a vacuum chamber, and then accelerated toward a target. It was confirmed that a beam current was considerably reduced in the process passing through the aperture; for instance, passing efficiency through the 120-mm aperture was on the order of 10^{-3}. This loss mainly results from the spreading of electrosprayed ions at atmospheric pressure.

When electrospraying is done in a vacuum, freeze and evaporation of a solution will be a serious problem. In other words, in the case of frequently-used solutions such as water and ethanol, it is difficult to achieve stable electrospraying in a vacuum because of the freeze and evaporation around a capillary tip. To solve the problem, we have proposed a vacuum electrospray beam source using pure ionic liquids for SIMS application. Ionic liquids have very low vapor pressure as well as high ionic condu ctivity; its use will ena ble us to perform stable electrospraying in a vacuum. We investigated the electrospray characteristics of an ionic liquid in a high vacuum environment with pressures around 10^{-5} Pa using the stainless-steel capillary. The experimental results demonstrated that stable electrosprayed currents of the order of 1000 nA can be continuously generated in both positive and negative modes. Experimental results indicate that the electrospray technique seems to be applicable to SIMS.

AS-TuP2 Structure and Chemical Composition of Thiol-SAMs on Au Surfaces for Biological Applications, *M. Bruns, S. Engin, V. Trouillet, D. Wedlich,* Karlsruhe Institute of Technology, Germany, *P. Brüner, T. Grehl, S. Kayser,* ION-TOF GmbH, Germany, *P. Mack, R.G. White*, ThermoFisher Scientific, UK

Structured and oriented immobilization of bio-molecules has become subject of great interest in recent years due to the expected diversity of applications, e.g. bio sensors in diagnosis, lab-on-chip technology, and modern cell culture focused on cell adhesion, migration, and differentiation. Therefore, a lot of effort has been spent to develop strategies for covalent and non-covalent immobilization of proteins, respectively. A very promising approach is surface patterning by micro-contact printing (μCP) to produce self-assembled-monolayers (SAMs) on gold surfaces based on mixtures of benzylguanine thiol (BGT) and matrix thiol. In this case BGT is the substrate for the SNAP-tag system, allowing for covalent attachment of any protein of interest fused to this tag, whereas the inert matrix thiol acts as spacer for BGT and moreover prevents from non-specific protein adsorption.1

The present contribution focuses on the characterization of pure benzylguanine and matrix thiols as well as mixtures of both using a combination of complementary surface analytical methods. For this purpose all SAMs were prepared on gold films deposited onto glass substrates by r. f. magnetron sputtering directly prior to the thiol exposure. The chemical composition and the covalent binding of the thiols were proved by time-of-flight secondary ion mass spectrometry (ToFSIMS) and X-ray photoelectron spectroscopy (XPS) as well. The orientation of the SAMs together with thickness information were achieved by high-sensitive low-energy ion scattering (LEIS),2and were justified by non-destructive depth profiles reconstructed from parallel angle-resolved XPS data applying a maximum entropy algorithm. Finally the μCP micro-structures were verified by ToFSIMS.

S. Engin, V. Trouillet, C. M. Franz, A. Welle, M. Bruns, and D. Wedlich, *Benzylguanine Thiol Self-Assembled Monolayers for Immobilization of SNAP-tag Proteins on Microcontact printed Surface Structures*, Langmuir, DOI: 10.1021/la904829y.

H. H. Brongersma, Th. Grehl, P. A. van Hal, N. C. W. Kuijpers, S. G. J. Mathijssen, E. R. Schofield, R. A.P. Smith, H. R.J. ter Veen, *High-sensitivity and high-resolution low-energy ion scattering*, Vacuum **84** (2010) 1005-7.

AS-TuP3 Thickness and Composition of the HfO2/Si Interface Layer As a Function of Aperture-Time of Oxidant-Agent for ALD-grown HfO2 Nanofilms, *P.G. Mani-Gonzalez, M.O. Vazquez-Lepe, A. Herrera-Gomez*, CINVESTAV Queretaro, Mexico

Hafnium oxide nanofilms were grown with ALD (Atomic Layer Deposition) on H-terminated Si(001) wafers employing TDMA-Hf (tetrakis dimetil animo hafnium) and water as precursors. The structure of the films was characterized with angle-resolved X-ray photoelectron spectroscopy (ARXPS). While the aperture-time for TDMA-Hf was kept constant at 0.08 s during the ALD deposition, the aperture-time (t H2O) for the oxidant-agent (H2O) was varied from 0 to 0.1 s among the different samples. The water exposition-time has a direct effect on the thickness of the HfO2 layer, which saturates at ~ 1.7 nm for 30-cycle ALD processes. The composition and thickness of the interface between Si and hafnia is approximately constant at Hf0.5Si0.5O2 and 1 nm for 0.02 < t H2O <0.06 s. For larger aperture-times, the Hf contribution to the composition rises slowly; the thickness of the layer also rises slowly. The total film thickness, including the hafnium silicate and hafnium oxide layers, saturates at ~ 3 nm. Our results are in accordance with prior results, which estimate the film growth rate at ~ 1 Å per ALD cycle.

AS-TuP4 Defect States in Amorphous GaInZnO Thin Film Grown on SiO$_2$/Si Substrates, *S. Heo, J.G. Chung, H.I. Lee, E.H. Lee, J.C. Lee, G.S. Park,* Samsung Advanced Institute of Technology, Korea, *J.S. Oh, H.Y. Cho,* Dongguk University, Korea, *D. Tahi, L.S. Son, S.K. Oh, H.J. Kang,* Chungbuk National University, Korea, *T. Nagatomi, Y. Takai*, Osaka University, Japan

Transparent oxide conductor and semiconductor are useful for us to develop electronic components in various applications such as flat panel display and solar cells. In particular, amorphous Ga-In-Zn-O (a-GIZO) thin films are promising channel materials for thin film transistors (TFTs) because a-GIZO TFTs exhibit large field-effect mobility (>10 cm2/V s) irrespective of their fabrication on various substrates, such as silicon, glass, plastic, polyimide, polyethylene terephthalate (PET), cellulose paper and flexible substrates. In addition, they have superior uniformity, low processing temperature, possibility of large-area deposition and long term stability, and moreover they are cost effective.

In recent years, a large progress has been made in high performance TFTs based on a-GIZO as channel layers. Amorphous semiconductors have defect states originating from structural disorder and defect, which strongly affect carrier transport properties and devices performances. However, fundamental material properties of a-GIZO such as the band alignment and defect states, which are important for devices structure and circuit configuration have not been investigated in detail so far. Moreover, any investigation of band alignment and defect states of a-GIZO thin films is very important to understand the transport mechanism and to improve device performances.

In this study, we have investigated the band gap, valence band offset and defect states of GIZO thin films by using reflection electron energy loss spectroscopy (REELS), X-ray photoelectron spectroscopy (XPS), thermally stimulated exo-electron emission (TSEE) and photoinduced current transient spectroscopy (PICT). The band gap and valence band offset (VBO or ΔE_V) allow us to determine the conduction band offset ΔE_C by using the relation: ΔE_C = Eg(SiO2) - ΔE_V (GIZO/SiO2/Si) - Eg(a-GIZO). The band gap is 3.2eV, and the conduction band offset of GIZO is 3.62 eV. The shallow defect states obtained via PICT were at 0.24eV and 0.53eV below the conduction band minimum of a-GIZO thin film, and the deep defect state obtained by means of TSEE is 1.827eV below the conduction band minimum of GIZO thin film.

AS-TuP5 Band Alignment and Defect States in Amorphous Si-N Compounds on Si Substrates, *H.I. Lee*, Samsung Advanced Institute of Technology

Silicon nitride (SiN$_x$) has an important application in the photovoltaics. First, plasma SiN films have provided effective surface passivation of silicon solar cells. Secondly, SiN has an important application in electronic memory devices. The memory property of the amorphous silicon nitride (a-SiN$_x$) is due to its electronic structure dominated by many deep traps.

Electronic properties of a-Si$_3$N$_4$ are determined mainly by deep traps of electrons and holes as well as by hollow traps responsible for the spreading of charges captured by deep traps. In other words, they are responsible for the degradation of nonvolatile memory devices based on NMOS. Because of this, a correct knowledge about the nature of levels is extremely

important in selecting the technology for the preparation of layers intended for specific application.

In this study, in order to obtain band alignment as well as defect state of SiN_x thin films, we have investigated the band gap and valence band offset with the variation in the composition of N contents by using reflection electron energy loss spectroscopy (REELS) and X-ray photoelectron spectroscopy (XPS), respectively. The defect states were investigated by using thermally stimulated exo-electron emission (TSEE), which have been specially designed for in-situ measurement of a defect state in analysis chamber without any electrodes.

Our result shows that the valance band offsets were increased from 0.033 eV to 1.24 eV with increasing N contents. The band gap was changed from 3.2 eV to 4.7 eV for the above materials. The defect state energy of the a-SiN_x films were observed at 1.85 eV by using thermally stimulated exo-electron emission. This energy is related to hydrogen migration or a dangling bond ($\cdot Si\equiv$), called the K center, in the silicon nitride.[1] The values of deep trap energy below the conduction band are independent of N content.[2] The defect state energy are properly assigned.

AS-TuP6   X-ray Degradation of Oxygen Plasma Treated and Chemically Reduced Poly(propylene) Surfaces in Comparison to Conventional Polymers*, T. Gross,* BAM Federal Institute for Materials Research and Testing*, W.E.S. Unger, G. Kühn,* BAM Federal Institute for Materials Research and Testing, Germany

X-ray induced sample damage during mono XPS analysis of an oxygen plasma oxidized and subsequently wet-chemically reduced poly(propylene) film was investigated as a example for plasma modified or plasma deposited samples. By doing this the degradation index approach as introduced by Beamson and Briggs in the Scienta ESCA300 high resolution XPS data base of organic polymers has been adopted. As to be expected the sample degrades by loosing oxygen as revealed by observation of decreasing O/C and C-OR/Csum ratios. However, the X-ray degradation indices are definitely higher than those of conventional reference polymers. Moreover, the C-OR/Csum degradation index is significantly higher in comparison to this one obtained for the O/C ratio. In that context there is no difference between the plasma sample and a conventional poly(vinyl alcohol) polymer. It is concluded that for reliable quantitative surface chemical analysis the quality of spectra in terms of acquisition times must be optimized aimed to a minimization of X-ray degradation. Finally it is proposed to describe the photon flux of a X-ray gun in an XPS experiment, which defines the degradation rate at the end, by using the sample current simply measured with a carefully grounded sputter-cleaned reference silver sample.

AS-TuP7   Analysis of Friction and Wear Mechanisms on Hard Coatings Deposited by Reactive Magnetron Sputtering*, J.S. Restrepo,* Universidad Autonoma de México*, M.F. Cano, J.M. Gonzalez, A. Ruden, F. Sequeda,* Universidad del Valle, Colombia

Different Hard coatings have been deposited (ZrN, CrN, TiN, TiZrN, TiAlN, AlSiN and multilayers systems) by DC Reactive Magnetron Sputtering at different deposition parameters (substrate temperature, Nitrogen flow, Voltage bias), to evaluate tribological properties with a ball on disc technique using different loads and speeds parameters to know the influence of this, on the tribological behavior. The ball on disc test was stopped at different distances to identify the wear mechanisms using a profilometer, scanning electron microscopy (SEM) and optical microscopy. These techniques allowed observed differents transitions on friction coefficient associated with the wear mechanisms. The rugosity polishing showed a low friction coefficient that increases slowly, the ploughing and scratching wear mechanisms were observed, producing unstable high friction coefficient and wear rate. Also different kinds of debris particles were observed like angular and roll shape.

AS-TuP8   Tribological and Mechanical Properties of Multilayer TiN/Cr_xN Coatings Deposited by Reactive Magnetron Sputtering*, F. Correa,* Universidad Autonoma de Occidente, Colombia*, M.F. Cano, J.M. Gonzalez, A. Ruden,* Universidad del Valle, Colombia*, J.S. Restrepo,* Universidad Autonoma de Mexico*, F. Sequeda*, Universidad del Valle, Colombia

TiN/CrxN multilayers, consisting of alternating nanometer-scale TiN and CrxN layers were deposited by the reactive magnetron sputtering technique on 4140 steel, the objective was studying the effect of bilayers numbers (period λ) on tribological and mechanical properties. The monolayer TiN and CrxN were also deposited in the same conditions and used as reference. Multilayers were characterized using x-ray diffraction (XRD), nanoindentation, scratch test and pin on disc testing. The hardness increased rapidly with the layer increase up to 110 bilayers and followed by a continuous decrease until 130 bilayers are achieved. Higher hardness corresponds to larger H3/E2 ratio, which is an indication of plastic deformation resistance. The coefficient of friction of the multilayers against

alumina ball counterpart is in the range of 0.81 to 1.10, lower than for a standard TiN (1.26). The lower coefficients of friction correspond to the enhancement of hardness and formation of the dense CrxYy oxide layer. To better understand the wear mechanism involved under dry sliding conditions of these multilayers, the worn surface of coating was analyzed using optical microscopy and profilometry. The anomalous wear rate behavior is explained by interfacial changes such as incoherent interface formation when the number of layers is higher, producing changes in the wear mechanism.

Key Words: Hard Coatings, Magnetron Sputtering, Multilayers, Wear mechanism

AS-TuP9   Multi-scale Characterization Studies of Li-ion Batteries*, S. Nagpure, B. Bhushan, S. Babu, G. Rizzoni*, The Ohio State University

Advanced Li-ion batteries with high energy and power density are fast approaching compatibility with automotive demands. While the mechanism of the operation of these batteries is well understood the aging mechanisms are still under investigation. While aging at the macroscopic level is directly measurable by increase in the internal resistance, at material level that include cathode, anode, separator and electrolyte aging can be attributed to many degradation mechanisms. As, the degradation of the material is caused by several simultaneous physiochemical processes that occur within the batteries, material characterization in automotive application batteries is a challenging task. We have identified and tested a set of experimental techniques for multi-scale characterization of the cathode in the Li-ion batteries. The electrical properties are studied using the electrochemical impedance spectroscopy and scanning spreading resistance microscopy. The structural degradation is studied using the infrared thermal imaging (meters), scanning electron microscope (micro), X-ray diffraction (micro), atomic force microscope (micro to nano), transmission electron microscope (micro) and electron energy loss spectroscopy. Finally, a relatively new neutron depth profiling technique was successfully used in these studies to study the transport and concentration of lithium within the few microns of the cathode thickness. We present the results obtained from this set of experiments when applied to the samples extracted from an unaged and an aged LiFePO4 based Li-ion battery.

AS-TuP10   Improved Tougaard Background Calculation using Predetermined Inelastic Electron Scattering Cross Section Functions K(T) using the Software UNIFIT 2011*, R. Hesse, R. Denecke*, Universität Leipzig, Germany

The shape of the background in x-ray photoemission spectra may be affected by secondary electrons and inelastic energy loss processes. A polynomial of low order has very often turned out to model the secondary electron background. The Tougaard background model [1] has been successfully used to characterise the inelastic loss processes. However, the correct usage of the Tougaard background needs a well defined K(T) function (T = energy loss). The introduction of a four parameter loss function $K(T) = BT/(C-C'T^2)^2+DT^2$ with the fitting parameters B, C, C' and D implemented in the fittable background function [2] allows the improved estimation of the K(T) function. The results will be compared with the recommended parameters by Tougaard. The calculation of inelastic electron scattering cross sections of clean surfaces from different materials using UNIFIT will be demonstrated.

[1] S. Tougaard, Surf. Interface Anal. 25 (1997) 137

[2] R. Hesse, T. Chassé, R. Szargan, Fresenius J. Anal. Chem., 365 (1999) 48

AS-TuP11   Comparative Study of Two Different Methods for Film Thickness Determination on Model and Real Systems using the Software UNIFIT 2010*, R. Hesse, P. Streubel, R. Denecke*, Universität Leipzig, Germany

The accuracy of thickness determination of laterally homogenous films by XPS in the range of few nm may be improved by combining two different methods. The results of the well established angle resolved photoelectron spectroscopy (**ARXPS**) for determining film thicknesses will be compared with the ones determined using the relative quantification of photoelectron lines at two different kinetic energies (i.e. energy-resolved) and the same emission angle (**ERXPS**). Only the substrate intensities were used. The advantages and disadvantages of both methods will be shown. The reliability and accuracy of the thickness determination by the two different methods is discussed for suitable model and real systems. The easy handling of the data analysis for estimating film thicknesses using UNIFIT will be demonstrated.

AS-TuP12 Non-destructive In-Depth Chemical Characterization of Air Exposed Plasma Polymers by Energy Resolved XPS, *P.-L. Girard-Lauriault*, *I. Retzko, S. Swaraj,* BAM Federal Institute for Materials Research and Testing, Germany, *N. Matsubayashi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan, *T. Gross, W.E.S. Unger*, BAM Federal Institute for Materials Research and Testing, Germany

Plasma polymers can be deposited on a wide range of substrates in order to introduce a desired surface chemistry intended for a wide range of applications. For many of these, only the chemistry of the outermost surface layer is relevant and therefore, many works have favoured the use of surface-specific techniques such as X-ray photoelectron spectroscopy (XPS) or time of flight secondary ion mass spectrometry (ToF-SIMS), which have various sampling depth under the surface. Recently, a technique enabling XPS depth resolution by the modulation of the photoelectron attenuation length for non-destructive chemical depth profiling, known as energy-resolved XPS (ERXPS), has emerged. In the best case, the minimum attainable 95 % information depth value is about 22 % of its value under standard Al Kα XPS conditions, thus permitting a better surface sensitivity than angle resolved XPS (ARXPS). ERXPS has also many other positive points that are thoroughly discussed.

In this study, plasma polymers containing oxygen and nitrogen based surface chemistries were prepared from allylalcohol, allylamine and acrylic acid. Established selective chemical derivatisation procedures with trifluoroacetic anhydride (TFAA) and 4-trifluoromethyl benzaldehyde (TFBA), are used to determine alcohols and amines, respectively. All samples were analysed by energy resolved XPS (ERXPS). By analysing the high resolution spectra we demonstrate that slightly aged plasma polymers prepared from allylalcohol and allylamine present a homogeneous in-depth chemistry in the range of XPS information depth (≈10 nm) while this was clearly not the case for their acrylic acid counterparts. Furthermore, it is shown that standard derivatisation reactions result in homogeneous changes of the chemistry in the above-mentioned information depth.

AS-TuP13 MVSA Analysis of 3D MCs$^+$ ToF-SIMS Data, *V. Smentkowski*, GE Global Research Center, *M.R. Keenan*, Consultant

Depth profiling via ToF-SIMS is a well established technique that is used to determine the depth distribution of trace species in samples. 3D depth profiling techniques are now being heavily utilized in the ToF-SIMS community since it enables the measurement of both the depth distribution and the lateral distribution of the species. 3D ToF-SIMS analysis are revealing that many samples are not uniform in the lateral dimension. Since a full mass spectrum is saved at every volume element, unexpected species are often found sub-surface, especially in real-world sample. Unfortunately, one often needs to perform two depth profile measurements in order to fully characterize a sample – a positive ion measurement to look for electropositive species with the highest sensitivity and a negative ion measurement in order to analyze electronegative species with the highest sensitivity. The two depth profile measurements are often performed using different erosion sources and experimental conditions which have been optimized for the species to be analyzed and often have significant differences in the erosion rate. Since the analysis are performed in two different regions of the sample, one can not correlate species observed in the two independent measurements. Additionally, there are instances where the amount of material is limited and one can not perform two measurements. MCs$^+$ analysis have been reported in the ToF-SIMS literature. For MCs$^+$ analysis one uses a Cs$^+$ ion beam to erode the sample, and a Bi$_3^+$ ion beam to perform the analysis in the positive ion polarity. Electropositive species are detected as M$^+$ and/or M+Cs$^+$ and the electronegative species are detected as M$^+$ and/or M+Cs2$^+$ (where M is the element being analyzed). In this paper, we will demonstrate, for the first time, the ability to analyze complicated 3D MCs$^+$ ToF-SIMS data sets using MVSA techniques. We will show the advantages of MVSA analysis over univariate analysis.

AS-TuP14 Metal Silicide Nanoscale Chemical Characterization with Scanning Auger Microscopy, *D.F. Paul*, *J.S. Hammond, D.G. Watson*, Physical Electronics

Scanning Auger Microscopy is a powerful compositional analysis technique for surfaces and nanostructures. It is well known that Auger instruments based on full CMA analyzers provide a stable imaging platform and analytical capability that can be successfully applied to a wide range of material systems. Recently a high energy resolution spectroscopy mode that provides enhanced chemical characterization was added to a CMA Auger instrument. This new functionality is integrated with the instrument while maintaining all the existing capabilities and benefits associated with the CMA based Auger instrument.

The usefulness of this new high energy resolution spectroscopy mode will be demonstrated with detailed chemical information from annealed metal

silicide ultra thin films on silicon wafers. Low energy ion beam depth profiling facilitates a chemical state evaluation of the silicide/wafer interface induced by the annealing process. Auger mapping and high energy resolution Auger spectroscopy also characterizes the three dimensional nanostructures formed on the surface and at the interfaces of these metal silicide ultra thin films.

AS-TuP15 Influences Finish Quality in Machining Austempered Ductile Iron, *W. Mattes*, SENAI-SC, Brazil, *A.C. Bottene*, LOPF/NUMA, Brazil, *R. da Silva*, UNERJ, Brazil

The austempered cast iron (ADI - Austempered Ductile Iron), has been successfully applied in diesel trucks, class 8 trucks and agricultural tractors power train parts. This material has also been used in high performance gears, applied in various segments of the mechanical industry, especially in the automotive field because of their properties and technical advantages associated to the combination of strength and ductility of the material. The main technical limitation of the ADI is attributed to its machinability. This problem is related to the hardening that occurs by the transformation of austenite, characteristic of the microstructure of austempered ductile, which affects the steps of the production process and achieve common cropping the part before the heat treatment and finish machining right after them. This paper discusses a study on the behavior of the surface finish quality, technical and financial feasibility of the machining process. Comparing the use of grinding, CBN wheel, and the hard turning operation, cemented carbide coated TiAlCrN, of ADI by comparative analysis of lifetime of the tools in terms of speed of cutting, using as a criterion to end the life of the tool flank wear of 0.3 mm.

AS-TuP17 Tougaard Background Parameters - Simpler Than One Might Expect, *P.J. Cumpson*, Newcastle University, UK

Several methods of calculating - or subracting - inelastic backgrounds from XPS spectra have been published over the years. Perhaps the most successful for practical XPS analysis has been the Tougaard background[1,2]. Tougaard proposed Universal Backgrounds that apply to most materials of analytical interest, yet are determined by only three or four parameters. In principle this allows the automatic removal of a large proportion of the inelatstic backround in many cases, but in practice there is often a problem in selecting appropriate Tougaard background parameters. These parameters do not have immediate physical interpretations, and it is often difficult to see which values are physically possible and which are not. Therefore it seems difficult, for example, to include all four of these parameters in a fit to an experimental spectrum; the fit would be ill-conditioned and underdetermined. The problem is made worse by the necessarily narrow energy ranges of backgrounds available for background fitting in practical applications.

We show that there are significant relationships between the four parameters in the Tougaard model, and connect these with materials parameters. The result is a background that depends upon a single parameter that can be included in a least-squares fit to any practical multi-element spectrum.

[1]. S. Tougaard og I. Chorkendorff, Differential Inelastic-Electron Scattering Cross Sections from Experimental Reflection-Electron Energy-Loss Spectra: Application to Background Removal in Electron Spectroscopy. Phys. Rev. B35, 6570 (1987).

[2] S. Tougaard, Universitality Classes of Inelastic Electron Scattering Cross Sections. Surface Interface Analysis, Vol 25, 137-155 (1997).

AS-TuP18 XPS Analysis of Surface Films Formed on Common Metals on Exposure to Ethanol-Blended Fuels, *H.M. Meyer III*, *S.J. Pawel*, Oak Ridge National Laboratory

Most automobile fuels contain some amount of ethanol, typically around 10% by volume, and fuels with higher ethanol levels are available. In Brazil mandated ethanol levels are 25% (E25 fuel) and in 2009 over 9 million vehicles were on the road using pure ethanol (E100) as fuel. Certainly, in the years ahead increasing levels of ethanol will be available in US fuels. As such, most automobile manufacturers are producing engines that can handle a variety of ethanol-blends. This poster examines several common metals used in fuel storage and fuel handing equipment, namely brass, galvanized steel, and nickel, and compares unexposed material to material that has been exposed to (1) reference gasoline and (2) E10 fuel and (3) E25 fuel. Samples were cleaned (acetone + ultrasonic), weighed, and placed in a stainless steel vessel. Fuel was added and the vessel was purged with Ar and sealed. After raising the temperature to 60 C, the samples were left for 28 days. Upon removal, the samples were rinsed with pure ethanol, dried, and weighed. X-ray photoelectron spectroscopy was used for determining surface composition. Sputter profiling was used to monitor changes in composition as a function of depth. For some samples, XPS mapping was

employed to determine lateral distribution of chemical species. Results presented in this poster clearly show greater oxidation and the formation of metal sulfide species for the ethanol-blended fuels as compared to the reference gasoline. Increasing the ethanol content above E10 to E17 showed an increase in the extent of oxidation and formation of metal sulfides.

AS-TuP19 Sputtering of Lunar Regolith Simulant by Singly and Multicharged Constituents of the Solar Wind, *F.W. Meyer, P.R. Harris, H.M. Meyer III*, Oak Ridge National Laboratory, *N. Barghouty, J.H. Adams, Jr.*, Marshall Space Flight Center NASA

We report preliminary results on sputtering of a lunar regolith simulant sample by H^+, Ar^+, Ar^{6+} and Ar^{9+} at solar wind-relevant energies. Such interactions are an important determinant of lunar exosphere composition, and may provide a possible pathway leading to the production of water on the moon. The presence of lunar water was recently confirmed by a number of orbiting lunar missions. The ions are generated using an electron cyclotron resonance (ECR) ion source at source potentials between 10-15kV. After being extracted, transported, and decelerated, the ions are normally incident on a pressed lunar regolith simulant sample that is situated within a floating UHV scattering chamber. The relative bias between the ECR source and the surface end station was adjusted to produce a constant impact energy of 0.375keV/amu for each of the 4 ion beams investigated. To simulate the effect of the dominant proton component, which constitutes >90% of the solar wind, the lunar regolith simulant sample was prepared by exposure to a proton beam up to total fluences of $\sim 2 \times 10^{18}$ H^+/cm^2 prior to each of the Ar beam sputtering runs. Both transient and steady state conditions of sputtered species were monitored by a quadrupole mass spectrometer situated within the UHV scattering chamber. SEM and XPS analyses of the JSC-1A AGGL simulant were performed to monitor possible changes in surface morphology and composition during the pressing of the loose powder into the sample holder.

AS-TuP20 Chemical Depth Profiling: Relating Interfacial and Sub-surface Characterization to Electrical Performance, *K.G. Lloyd, L. Zhang, J.P. Wyre, J.R. Marsh, M.A. Plummer*, DuPont Corporate Center for Analytical Sciences

Thin multi-layered structures form the basis for photovoltaic/solar cells, OLED displays, and many other electronic devices. Electrical performance can be influenced by the thickness of these layers, the widths of interfaces between layers and/or development of interfacial chemistry, and the extent and location of dopants within layers. Depth profiling, i.e., obtaining chemical information as a function of dpeth, can provide this information, especially for systems wehre cross-sectioning is not an option, species of interest are present below 1%, or sampling with better than 1 micron depth resolution is required.

ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) and X-ray Photoelectron Spectroscopy (XPS, a.k.a. ESCA) are typically used in conjunction with a high-current ion sputter beam to analyze the outermost surfaces as they are freshly revealed. ToF-SIMS depth profiling offers high mass resolution, spatially-resolved chemical information, and the collection of the entire mass spectrum at each depth interval. The combination of ToF-SIMS depth profiling and multivariate methods of data analysis allows better definition and characterization of interfacial regions between layers.

Examples include characterization of the BSF (back surface field) layer on solar cell backsides, monitoring layered oxide growth on annealed stainless steels, and study of interdiffusion in organic electronic layered structures.

AS-TuP21 In-situ XPS Analysis of Co and Co^{2+} during Steam Reforming of Ethanol on Supported Cobalt Catalysts, *A. Karim, Y. Su, M.H. Engelhard, D. King, Y. Wang*, Pacific Northwest National Laboratory

In catalysis, the oxidation state of metal nanoparticles on the surface is often unknown, especially under oxidizing conditions. The redox properties of the catalyst are typically investigated by temperature programmed reduction and oxidation or x-ray absorption spectroscopy. However, these are not the surface sensitive techniques and provide limited surface details especially under H_2/H_2O environments. We report the use of in-situ x-ray photoelectron spectroscopy (XPS) to determine the oxidation state of Co following exposure to O_2, H_2, and H_2/H_2O. We found that the type of support and catalyst pretreatment (calcinations and/or reduction temperature) have a strong effect on the Co^0/Co^{2+} ratio. Our results indicate that Zn helps stabilize Co against oxidation by O_2 or H_2O. The in-situ XPS measurements allowed us to study the effect of Co^0/Co^{2+} ratio on the catalytic activity and understand the role of Co^{2+} in the ethanol reforming reaction pathways. The catalytic tests show that both Co^0 and Co^{2+} were active in the C-C bond cleavage and water gas shift reactions. However, Co^0 is shown to be much more active than Co^{2+}. Also, the reaction pathways for CO_2 and CH_4 formation appear to be different on Co^0 and Co^{2+}. Catalysts with higher Co^0/Co^{2+} surface ratio exhibited lower selectivity to CH_4. Our results show that ethanol decomposition and CO methanation are more

favored on Co^{2+} relative to Co^0. In addition, we show that on both Co^0 and Co^{2+}, CO_2 is a secondary product forming by the water gas shift reaction.

AS-TuP22 Surface Characterization of Al-Si-Fe-X (X = none, Sb, V) Rapidly Solidified Ribbons, *V.N. Gaidarova*, Bulgarian Academy of Sciences, Bulgaria, *Y.T. Yordanov*, Sofia Technical University, Bulgaria

Al-Si alloys are used in the automotive industry. Improvement of their properties is achieved by rapid solidification (RS) [1]. Highly developed surface of RS material is of importance in both interaction with the environment and processing of materials during ingots production. Surface formation and development under thermal treatment depends on the alloying and modifying elements.

Al-Si under-eutectic alloys with addition of Fe, Sb, V in different combinations are produced by RS using Planar Flow Casting technique. As-cast and thermally treated samples are studied using Auger Electron Spectroscopy (AES) combined with argon ion sputtering.

AES depth profiles of as-cast specimens demonstrate formation of nanoscale aluminum based oxide, enriched layer (EL) with solute elements and a region of constant Al/Si content following in depth. Annealing up to moderate temperatures ($\leq 638K$) causes changes in thickness of both oxide scale and EL. Availability of Fe ($\leq 2wt.\%$) promotes diffusion of solute elements in oxide and EL while addition of Sb, even in a minor quantity 0,17 wt.%, to the last alloy content decreases Si-segregation. Changes are not detected in the oxide or EL of (Fe+V) doped RS ribbons. Annealing up to temperatures $\geq 673K$ leads to ceasing of oxidation and diminishing of silicon enrichment for all studied Fe-containing RS alloys. These remarkable changes of elements distribution can be connected with crystallization of Fe-containing phase at oxide/bulk interface and growth of silicon precipitations. Registered solute enrichment is in agreement with the segregation prediction [2], which is based on the phase diagrams of alloys. Comparison with micro hardness measurements on the surface of the ribbon samples shows proportional dependence on the uniform distribution of the fine silicon precipitations. With their growth the micro hardness declines, excluding for the RS alloy doped with Fe+V. In the last case dopands content does not allow iron segregation at the surface, which evidently leads to hardening by finely dispersed Fe-containing particles in the Al-matrix under.

References:

[1]. E. Lavernia, J. Ayers, T.S. Srivatsan, Int. Materials Rev. 37(1992)1.

[2] J.J.Burton, E.S.Machlin, Phys. Rev. Lett., 37(1976)1433.

AS-TuP23 Characterization of a Self-assembled Molecular Nanolayer at Buried Cu-silica Interface, *S. Garg, R. Teki, A. Jain, K. Chinnathambi, B. Singh*, Rensselaer Polytechnic Institute, *V. Smentkowski*, GE Global Research Center, *M. Lane*, Emory and Henry College, *G. Ramanath*, Rensselaer Polytechnic Institute

Integration of metal-dielectric interfaces using molecular nanolayers (MNLs) is attractive for prospective applications such as laminates in high frequency electronics and packaging, nanodevice wiring and composites. Recent works have shown that annealing-induced siloxane bridging can toughen organosilane-functionalized copper-silica interfaces. While strong bonding of the MNL with the under- and over-layers is essential for promoting adhesion, the nature of the MNL structure and bonding, especially at temperatures where the MNLs are known to degrade on bare surfaces, are unclear. But tracking atomic-level intermixing and interfacial phase formation in a sub-nm-layer is an exacting challenge due to difficulties in distinguishing Si atoms in the organosilane MNL from Si atoms in the silica substrate, and obtaining sufficient contrast by electron microscopy. Here, we study organogermane-tailored interfaces using a combination of electron spectroscopy and microscopy, and density functional theory calculations to obtain insights into the interface chemical changes. Our results reveal that annealing decomposes the organic monolayer into an inorganic Cu-O-Si network, leading to interface toughening.

We assembled Benzyl-trichlorogermane (BTCG) on silica to form a 0.7-nm-thick nanolayer. Four-point bending fracture tests on as-prepared $Cu/BTCG/SiO_2$ sandwiches revealed a low interface toughness of 2.1 J/m^2, comparable to pristine Cu/SiO_2 structures. However, interfacial toughness increased monotonically with annealing temperature, yielding values as high as 23.3 J/m^2 for $T_{anneal} = 500$ ºC. Core-level spectra from silica fracture surfaces show a strong Ge signature for $T_{anneal} \leq 300$ ºC that becomes undetectable for $T_{anneal} \geq 400$ ºC, suggesting Ge transport and destruction of the organic MNL. This result is corroborated by time-of-flight secondary ion mass spectroscopy (SIMS) profiles showing the smearing of the interfacial Ge spike into the silica layer upon annealing. Incorporation of Ge

in the silica weakens the Si-O-Si network, leading to intermixing of Si, O and Cu, forming nanoscale islands of rhombohedral $CuSiO_3$ observable by cross-sectional transmission electron microscopy and X-ray spectroscopy. For pristine Cu/SiO_2 structures there were no changes at the interface and the toughness value was ~ 3 J/m^2 for $T_{anneal} \leq 700$ °C. Our findings suggest that molecular degradation of the organic MNL to form nanoscopic layer of inorganic metal-oxide-silicon bonds could be an attractive approach for toughening interfaces.

AS-TuP24   Experiences with the High Energy Resolution Optics (HERO) Update on a Physical Electronics 690 Auger System, *W. Wallace, J.A. Ohlhausen, M.T. Brumbach*, Sandia National Laboratories

We will present our experiences with the new High Energy Resolution Optics (HERO) upgrade on a Physical Electronics Auger 690 system. This upgrade allows the single pass cylindrical analyzer in the Auger system to achieve higher energy resolution than in the standard mode. With this upgrade, it should be possible to separate chemical states for certain elements. Also, it should be possible to separate closely spaced peaks from selected elements that have been difficult or impossible to separate without the upgrade. Specifically, we will investigate practical use of this upgrade in the analysis of materials systems where overlapping peaks have historically been an issue, such as Kovar, which consists of the elements Ni, Fe and Co. Strategies for the successful use of the technique as well as its current limitations will be shown.

AS-TuP25   A Device for Traceable Force Probe Calibration, *J.F. Portoles, P.J. Cumpson*, Newcastle University, UK

AFM has become in the last two decades an instrument for the measurement of forces in the piconewton range, including forces at the single molecule level. Although many methods have been developed for the force calibration of AFM cantilevers [1], these use to be affected by high uncertainties and sometimes difficulty of use. Furthermore there is a growing need for a traceable force calibration standard that provides traceability to the units of the SI [2] and therefore allows comparison between instruments and with related force measurement techniques such as the Optical Tweezers and the Biomembrane Force Probe. We present the development of a device that provides fast and easy force calibration of AFM cantilevers and other force probes, simultaneously facilitating the dissemination of force and providing traceability to the units of the SI.

[1] J.L. Hutter and J. Bechhoefer, Rev. Sci. Instrum. 64 (7) 1993, pp. 1868-1873

[2] P.J. Cumpson and J. Hedley, Nanotechnology 14 (12) 2003, pp. 1279-1288

AS-TuP26   Synthesis and Characterization of System $Sr(Ru_{1-x}Fe_x)O_3$ type Perovskite, *L. Huerta, J.L. Mazariego, M. Quintana,* Universidad Nacional Autónoma de México, *E. Ramírez,* Universidad Autónoma de la Ciudad de México, *M. Flores,* Universidad de Guadalajara, México, *R. Escamilla*, Universidad Nacional Autónoma de México

Polycrystalline samples of the $SrRu_{1-x}Fe_xO_3$ system with x = 0, 0.25, 0.5, 0.75 and 1.0, were synthesized by solid state reaction of stoichiometric quantities of oxides of RuO_2, Fe_2O_3 and $SrCO_3$. The samples were characterized by X-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and ac magnetization vs. temperature measurements. XRD results shown that the lattice parameter decreases with the iron content; as a consequence the unit cell volume decreases. The Sr 3d, Ru 3d Fe 3d and O 1s spectral lines associated to the chemical states of $Sr(Ru_{1-x}Fex)O_3$ were identified by XPS. Curves of ac magnetization vs. temperature shown for x $\geq$ 0.25 a behavior spin glass.

AS-TuP27   Surface Energy, Topography & Composition of SiOx on Polycarbonate by Proton-Induced X-ray Emission (PIXE), Atomic Force Microscopy & Sessile Drop Contact Angle Analysis using Young-Dupre Equation., *Q.B. Xing,* Arizona State University, *C.F. Watson,* SiO2 Associates, LLC, *M.A. Hart, D.A. Sell, J.D. Bradley,* **R.J. Culbertson**, *A.S. Benitez-Brady,* Arizona State University, *B.J. Wilkens,* LeRoy Eyring Center for Solid State Science at Arizona State University, *N. Herbots*, Arizona State University

The surface energy of silica is correlated with topography and composition in micron thick films on polycarbonate visors for football, hockey, ski and scuba diving.

Use of visors can be limited by condensation that occurs in during athletic performance. Control of the hydro-affinity of the surface requires an understanding of hydrophobic/hydrophilic behavior as well as of condensation kinetics and surface contamination for up to several continuous hours

Combining Proton-Induced X-ray Emission (PIXE), Tapping Mode Atomic Force Microscopy (TMAFM) & the Sessile Drop Method with Contact Angle Analysis (CAA) using Young-Dupre Equation, yields insights into nucleation and ripening of water droplets. Real-time observation via optical microscopy of both reflected and transmitted light, PIXE, TMAFM and CAA with previous Rutherford Backscattering Spectrometry (RBS) results ca establish a model to predict surface energy and hydro-affinity of silicates, phospho-silicates and other compounds used for high impact resistance vision wear coatings. Ultimately, the goal is to control condensation on such coated polymers for applications in sport eyewear used in hockey, skiing, football and other contact sports, swimming goggles, and diving masks.

Surface characterization techniques in this research combine the 4.265 ± 0.035 MeV 12C(alpha, alpha)12C and the 3.05 ± 0.005 MeV 16O(alpha, alpha)16O MeV Oxygen Nuclear Resonance to increase light atoms detection with 2.8 MeV Hydrogen Elastic Recoil Detection for compositional analysis with depth profiling, and Tapping Mode Atomic Force Microscopy for surface topography. The water affinity of the solid surface is measured via contact angle analysis using the Sessile Drop method calibrated with standards such as OH(1x1)Si(100), 100 nm thermal oxides on Si(100), Si(100) amorphized by high dose Si ion implantation at 35-175 keV, alpha-quartz crystals, and the Young-Dupré equation to compute surface energy. The surface energy is then correlated with statistical analysis of Tapping Mode Atomic Force Microscopy topographs and PIXE/RBS analysis to predict and determine the mechanism and kinetics of water condensation. Polymer adsorption on these surfaces is used to alter the surface hydroaffinity and maintain clarity when condensation occurs by making it hydrophilic [1].

[1] US Patent pending "Molecular films for controlling hydrophobic, hydrophilic, optical, condensation and geometric properties of Si-based surfaces. Inventor(s): N. Herbots, J. D. Bradley, M. A. Hart, D. A. Sell, S. D. Whaley, Q. Bradley (filed: November 9, 2009)

AS-TuP28   An Investigation of Primary Ion Choices in Depth Profiling Using Time-of-Flight Secondary Ion Mass Spectrometry, *Z.H. Zhu, V. Shutthanandan*, Pacific Northwest National Laboratory

Depth profiling is one of the important applications of time-of-flight secondary ion mass spectrometry (ToF-SIMS). Dual beam depth profiling strategy is commonly used because the current of the primary ion beam is normally very weak (~10^{-12} A), and the second beam with high current (10^{-8}-10^{-6} A) is introduced for sputtering. Recent years, a major development in ToF-SIMS field is application of cluster primary ions. It has been found that cluster primary ions can dramatically enhance signal intensity of molecular ions with a factor of 10-1000. So far, cluster primary ions have been introduced into commercial ToF-SIMS instruments for over five years. However, in presently available commercial ToF-SIMS instruments, the usable currents of cluster primary ion beams are considerably smaller than that of monatomic primary ion beams. More importantly, enhancements using cluster primary ions are not only material-dependent but also ion species-dependent. Therefore, large amounts of experimental data are needed to develop an understanding of how to choose an optimal primary ion for ToF-SIMS depth profiling.

In this work, we studied depth profiling of several representative systems: (1) Hydrogen depth profiling in silicon wafer, zinc oxide crystal and normal glass; (2) molecular depth profiling of a thin sucrose film on silicon substrate; (3) molecular depth profiling of Irganox "delta" layers prepared by NPL, United Kingdom . Six primary ion beams (25 keV Bi^+, Bi_3^+, Bi_5^+, 50 keV Bi_3^{++}, 10 keV C_{60}^+ and 20 keV C_{60}^{++}) were compared. Our data show that enhancement of cluster primary ions for elemental species is limited (~1.5-4.0 times) if compared to that for molecular species (>>10 times). Considering the highest usable currents of difference primary ion species on presently available commercial ToF-SIMS instruments, we suggest that monatomic primary ion beams may be the best choice for elemental depth profiling, and cluster primary ion beams are better choices for molecular depth profiling.

Applied Surface Science
Room: Cochiti - Session AS-WeM

New Ion Beam Technologies for Imaging, Sample Preparation and Analysis
Moderator: J.A. Gardella, Jr., SUNY at Buffalo

8:00am **AS-WeM1 Ion Photon Emission Microscopy: A Novel Method for Studying Radiation Effects**, *J.V. Branson, K. Hattar, G. Vizkelethy, C.J. Powell,* Sandia National Laboratories, *P. Rossi,* University of Padua and INFN, Italy, *B.L. Doyle*, Sandia National Laboratories

The development of a new radiation effects microscopy (REM) technique is crucial as emerging semiconductor technologies demonstrate smaller feature sizes and thicker back end of line (BEOL) layers. To penetrate these materials and still deposit sufficient energy into the device to induce single event effects, high energy heavy ions are required. Ion photon emission microscopy (IPEM) is a new technique that utilizes coincident photons, which are emitted from the location of each ion impact to map out regions of radiation sensitivity in integrated circuits and devices, circumventing the obstacle of focusing high-energy heavy ions. The (x,y) coordinates are instead determined with a single photon, position-sensitive detector. Thus, a high energy broad beam can be used to achieve high LETs, while still mapping out radiation-sensitive regions with sufficient resolution. Several versions of the IPEM have been developed and implemented at Sandia National Laboratories (SNL). The initial IPEM was a tabletop system, which utilized a Po-210 alpha source as the incident radiation. The second version has been utilized on the microbeam line of the 6 MV tandem accelerator at SNL, which allows for direct results comparisons between data obtained with a scanned, focused microbeam, and that from IPEM. Another IPEM was designed for ex-vacu use at the 88" cyclotron at Lawrence Berkeley National Laboratory (LBNL). That facility allows for the use of a heavy ion cocktail, with beam energies up to several GeV. Extensive engineering is involved in the development of these IPEM systems, including resolving issues with electronics, event timing, optics, phosphor selection, and mechanics. The various versions of the IPEM and the obstacles, as well as benefits associated with each will be presented. In addition, the current stage of IPEM development as a user instrument will be discussed in the context of recent results.

*Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a wholly-owned subsidiary of Lockheed Martin company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:20am **AS-WeM2 Synthesis and Characterization of Gold Nanocluster-Cavity Pairs in SrTiO$_3$**, *S.V. Shutthanandan, C.M. Wang, B. Arey, W. Jiang, Y. Zhang, T. Thevuthasan,* Pacific Northwest National Laboratory, *G. Duscher*, Oak Ridge National Laboratory

Dispersion of gold nanoclusters in single crystal TiO_2, MgO, and $SrTiO_3$ have been found to influence the optical properties of the materials. One way to make these clusters in these oxide media is through Au ion implantation followed by annealing at high temperatures for extended period of time. The Au clusters generated by this ion beam synthesis method often associated with vacancies as a cluster-vacancy pair in the matrix. These nanometer scale vacancy clusters are generally called quantum antidotes and they are believed to be spatially located at the interface between the Au clusters and the matrix. To verify this proposition, Au nanoclusters dispersed in $SrTiO_3$ single crystals were prepared using ion implantation at 975 K and subsequent annealing at 1275 K for 10 hours. We have used a suite of imaging capabilities including newly developed Helium ion microscopy (HIM) and scanning transmission electron microscopy (STEM) with high-angle-annular-dark-field (HAADF) imaging to understand the structural properties and spatial distribution of the Au and vacancy clusters. The results indicate that gold nanocluster-cavity pairs were formed uniformly throughout the implanted region. Size of the Nanocluster-cavity pairs ranges from 5 to 30 nanometers. In cluster free regions where the Au concentration is low, the HADDF results clearly indicate the substitution of Au for cations. The Au clusters and the cavity show spatial association, indicating a strong interaction during their respective clustering process.

9:00am **AS-WeM4 Material Contrast Mechanisms in FIB and SEM Images**, *L.A. Giannuzzi,* FEI Company, *M. Utlaut*, Portland State University

The relative contrast of both FIB and SEM images in metals yield a non-monotonic function with target atomic number. Material contrast from FIB images is similar to the material contrast observed from SEM images, with differences that can be directly attributed to particle-solid interaction theory. The non-monotonic particle stopping power and the sputter yield (for those particles that cause sputtering) are directly responsible for material contrast. The term "Z-contrast" is shown to have a different meaning than universally understood.

9:20am **AS-WeM5 A High Brightness Plasma Source for Next Generation FIB, SIMS and Surface Engineering**, *N. Smith, P.P. Tesch, N.P. Martin, R.W. Boswell*, Oregon Physics **INVITED**

Milling speeds with a gallium focused ion beam (FIB) are often much too slow for many sample preparation and surface engineering applications. For example, cross-sectioning stacked-die semiconductor devices, prototyping micro-mechanical structures and delayering IC's for circuit mapping are growing applications that require a milling rate that far exceeds that provided by the gallium FIB.

Furthermore, secondary ion mass spectrometry (SIMS) imaging has been limited to a lateral resolution of 200nm when using an oxygen focused ion beam for high sensitivity surface analysis. Many applications in material science could benefit from an ability to image trace level surface chemistry with <20nm resolution. Example applications include, sub-cellular imaging of trace metals in the brain for neurodegenerative disease studies, analysis of trace element segregation in metal alloys and studying isotope distributions in meteorites and interplanetary dust particles.

In the more general area of direct-write surface engineering, precision milling and deposition with nanometer precision is limited to volumes of <10^{4}um^3 when using gallium FIB systems. Also, engineered devices must generally be tolerant of high gallium concentrations being implanted in the near-surface region. These are major restrictions when fabricating devices that require nanometer precision across dimensions of several hundred micrometers. Additionally, inherent gallium implantation can render structures bio-incompatible and compromise the electrical properties of many materials.

Here, we review a plasma ion source technology (Hyperion^{TM}) that can provide a focused ion beam capable of milling silicon at a rate of >5000um^3/s with <4um milling resolution and <20nm imaging resolution with 30keV xenon ions. The same ion source is also readily operated as a high brightness source of oxygen, hydrogen and any inert ions.

By transferring energy to plasma electrons via a RF induction field, it is possible to create a plasma state without a cathodic electrode. This approach can create high plasma densities (>1x10^{13} ion cm^{-3}), with very low mean thermal ion energies (<0.05eV), providing the conditions for an energy normalized beam brightness that now exceeds 1x10^4 Am^{-2}sr^{-1}V^{-1}. This high brightness can be attained with long lifetimes (>>2000 hours), stable beam current (<±0.5% drift per 30 minutes) and an axial energy spread for the extracted beam of 5-6eV and for an array of ion species.

This paper presents FIB and SIMS data from this new ion source. The operating principles of the ion source, the properties of the beam(s) being created and the projected future for this technology are also described.

10:40am **AS-WeM9 XPS Comparison of Ar, Coronene, C$_{60}$, and Ar Gas Cluster Ion Beam Depth Profiling of Polyimide Films**, *J.S. Hammond,* Physical Electronics, *T. Miyayama, N. Sanada,* ULVAC-PHI, Japan, *J.F. Moulder,* Physical Electronics, *M. Suzuki,* ULVAC-PHI, Japan, *A. Takuhara,* Kyushu University, Japan

Polyimide thin films have found wide-spread use in many industrial products such as microelectronics and thin film display panels due to their excellent insulating properties, high resistance to heat in manufacturing processes and its excellent flexibility and other mechanical properties. To increase the adhesion of metal films to polyimide substrates, ion beam and plasma surface modification steps are frequently incorporated in the manufacturing processes. It is therefore highly desirable to find a quantitative chemical depth profiling technique to characterize the surface modification layer and the polyimide thin film itself. A comparison of the use of XPS depth profiling of thin polyimide films with Ar, Coronene, C$_{60}$, and Ar Gas Cluster Ion Beam (GCIB) sputter sources will be presented. The GCIB sputter source produces an Ar$_{2,500}^+$ ion beam with user definable incident beam energy. XPS elemental quantification and chemical state spectroscopy reveals that Ar, Coronene and C$_{60}$, ion sources produce rapid damage of the polyimide with a wide range of ion gun experimental conditions. Optimized conditions for the incident ion beam energy of the GCIB will be presented to provide minimal chemical state damage during the depth profiling of 100 nm thick films. Results will also be presented showing that the GCIB source can be used to remove Ar$^+$ induced damage layers.

11:00am AS-WeM10 XPS Sputter Depth Profiling of Organic Materials Using a Coronene Ion Source, *S.J. Hutton, C.J. Blomfield, A.J. Roberts, G. Mishra, I.W. Drummond, S.C. Page*, Kratos Analytical Ltd., UK

11:20am AS-WeM11 The Application of Digital Techniques to the Calibration of Depth Scales in XPS Sputter Profiling, *P. Mack, T. Nunney, R.G. White, A. Wright*, ThermoFisher Scientific, UK

When sputter profiling a multi-layer material using XPS, it is often difficult to obtain an accurate calibration of the depth scale. In part, this is due to the fact that the sputter rate in each material is different and a post profile measurement of crater depth will only yield an average value for the sputter rate. The purpose of this paper is to provide a method for an internal, standardless calibration of the depth scale which can be applied to single profiles through multilayer materials.

As a layer is etched to a thickness of a few nanometres, the spectrum from the underlying layer can be seen. With knowledge of the electron attenuation lengths in the layers it is then possible to calculate the thickness of the remaining upper layer. If this calculation is carried out following each of a number of sputter cycles then the sputter rate within the layer can be calculated. This value can then be applied to sputtering within the whole of the upper layer. If this is repeated for each layer in a multilayer sample then an accurate depth scale can be constructed.

This method will be applied to a number of samples including standard multilayer materials and the value of the method assessed.

In Situ Microscopy and Spectroscopy Topical Conference
Room: Acoma - Session IS+AS+NS+MI-WeM

In Situ Microscopy/Spectroscopy – In Situ Nanoscale Processes
Moderator: A. Mkhoyan, University of Minnesota

8:00am IS+AS+NS+MI-WeM1 Low-dimensional Superconductivity of Pb Nanostructures, *J. Kim, H. Nam, G.A. Fiete, C.K. Shih*, The University of Texas at Austin

The influence of low-dimensional geometries on superconductivity is an important issue to study because in low dimensions it is key to understanding coherence and robustness of the superconducting state in quantum-mechanically confined geometries. The lateral size dependence of superconductivity on 2 dimensional Pb islands is studied by using *in-situ* low temperature Scanning Tunneling Microscopy/Spectroscopy (STM/S). The superconducting transition temperature (T_c) of each island is obtained by fitting the STS data with a BCS-like density of states. It is found that superconductivity shows a clear dependence on the Pb island lateral size even when it is larger than the bulk coherence length (~80nm), and it is also found that T_c drops very quickly below a certain lateral size. In addition, an intriguing lateral proximity effect is observed at the interface of different local superconducting regions of Pb islands. Current imaging tunneling spectroscopy (CITS) is used to visualize this proximity effect in real space.

8:20am IS+AS+NS+MI-WeM2 Enabling the Measurement of In-Situ, Site-Specific Mineral Transformation Rates in Supercritical CO_2 through Development of a High Pressure AFM, *S. Lea*, Pacific Northwest National Laboratory, *S.R. Higgins,* Wright State University, *K.G. Knauss,* Lawrence Berkeley National Laboratory, *K.M. Rosso*, Pacific Northwest National Laboratory

Capture and storage of carbon dioxide in deep geologic formations represents one promising scenario for minimizing the impacts of greenhouse gases on global warming. At issue is the ability to demonstrate that CO_2 will remain stored in the geological formation over the long-term and so knowledge of mineral-fluid transformation rates is critical for this determination. The majority of previous research on mineral-fluid interactions has focused primarily on the reactivity of minerals in aqueous solutions containing CO_2. However, caprock integrity would be dictated primarily by mineral interaction with supercritical CO_2 ($scCO_2$) as the buoyant phase slowly displaces or dessicates residual aqueous solution at these surfaces. Many of the mechanisms of mineral interfacial reactions with hydrated or water-saturated CO_2 are unknown and there are unique challenges to obtain kinetic and thermodynamic data for mineral transformation reactions in these fluids.

A high-pressure atomic force microscope (AFM) is currently under development that will enable *in-situ* site-specific measurements of metal carbonate nucleation and growth rates on mineral surfaces in contact with $scCO_2$ fluids. This apparatus is based on the hydrothermal AFM that was developed by Higgins et al.[1], but includes some enhancements and is designed to handle pressures up to 1500 psi. The noise in our optically-based cantilever deflection detection scheme is subject to perturbations in the density (and therefore index of refraction) of the compressible supercritical fluid. Consequently, variations in temperature and pressure within the fluid cell can have a significant impact in our ability to discern atomic steps on mineral surfaces. We demonstrate with our test fluid cell that the equivalent rms noise in the deflection signal is similar to (and in some cases less than) the equivalent noise for an AFM in its 'standard configuration' under controlled pressures of ~80 bar and temperatures of 60-80 °C and therefore *in-situ* atomic scale imaging of mineral surfaces in $scCO_2$ should be possible. This talk will also focus on recent progress in the development of this instrumentation, which will enable a unique platform for elucidating the role of water in mineral transformations, providing a means for determining effective kinetic constants.

1. Higgins, S. R.; Eggleston, C. M.; Knauss, K. G.; Boro, C. O., A hydrothermal atomic force microscope for imaging in aqueous solution up to 150°C. *Review of Scientific Instruments* **1998,** *69* (8), 2994-2998.

8:40am IS+AS+NS+MI-WeM3 Au on VLS-grown Si Nanowires: Spreading of the Liquid Metal Seed, *E. Dailey, P. Madras, J. Drucker*, Arizona State University **INVITED**

In situ TEM shows that liquid AuSi spreads from the seed along the NW sidewalls to form a thin liquid sheath for some growth conditions. The thin liquid film phase separates to form small solid Au clusters when the NW is cooled below the solidus temperature. Quantitative composition maps show that the Au composition is highest near the NW tip. The thickness and length that the liquid film spreads from the seed is growth condition and NW diameter dependent and represents a steady state during growth. These observations can be related to the spreading thermodynamics of liquid droplets along cylinders. Growth conditions for which the liquid AuSi spreads from the seed stabilize 'vertical' growth along <111> by lowering the surface energy of the high-energy {112} bounding facets. In contrast, the NWs kink toward <112> when grown using conditions that favor growth with Au-free sidewalls since these NWs are bound by facets that are found on the Si equilibrium crystal shape.

9:20am IS+AS+NS+MI-WeM5 Advanced Study of Nanoscale Mechanisms: Plans for In-Situ TEM Microreactor, Gas Cell, and Multi-Beam Irradiation Experiments, *B.G. Clark*, *K. Hattar,* Sandia National Laboratories*, D. Nackashi, J. Damiano, S. Mick,* Protochips, Inc.*, B.L. Doyle*, Sandia National Laboratories

Over the years, in-situ TEM experiments have allowed for observation of material mechanisms at high resolution and in real time; a feat often not possible with any other experimental technique. With increasing demand for understanding nanoscale material mechanisms, both with growth in the applications of nanomaterials and in the development of predictive materials models based on experimental observation, the realm of in-situ TEM experiments has continued to expand. Highlighted in this presentation will be the development of three, exciting new capabilities for in-situ TEM experiments at Sandia National Labs.

The first part of the talk will focus on the development of two new in-situ TEM stages. Expanding on the success of static and single inlet-outlet liquid cells, we are designing a new in-situ TEM microreactor liquid cell with the capability to mix fluids in controlled temperature regimes, to view reactions as a function of time, and to capture and analyze reaction products. Research programs using this stage will pursue studies of self-assembly, directed assembly, and nanoparticle formation and growth. In addition, for observation of advanced degradation of materials in the presence of gases and/or vapor, a new in-situ TEM gas cell stage is being developed. This stage will have the capability to study a variety of gas-solid and vapor-solid interactions, such as corrosion, oxidation, and hydriding, with accurate control over temperature and pressure. Envisioned research will include understanding environmental degradation of materials during storage of spent nuclear fuels, an issue of critical importance for the future of nuclear energy.

The second part of the talk will highlight the development of a new, triple-ion-beam in-situ irradiation TEM. By combining expertise in in-situ TEM experiments with expertise in ion beam studies, planning is currently underway that would culminate in the construction of an instrument capable of studying the effects of bombardment by up to three ion beams simultaneously within the TEM. This unique, triple-ion-beam capability would enable advanced experiments such as real-time studies of neutron induced damage and transmutation in a fission/fusion reactor by combining Fe, He, and H ions.

company, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

9:40am IS+AS+NS+MI-WeM6 *In Situ* TEM Investigation into the Thermal Stability of Nanograined FCC Metals and Alloys, *K. Hattar*, *B.G. Clark*, Sandia National Laboratories, *J. Kacher*, University of Illinois at Urbana-Champaign, *J.A. Knapp, D.M. Follstaedt, L.N. Brewer*, Sandia National Laboratories, *I.M. Robertson*, University of Illinois at Urbana-Champaign

Nanostructured materials often display very unique properties related to their far-from-equilibrium nature. Due to these unique structures, many of these materials transform into other, more stable microstructures with minimal thermal excitation. This work will highlight examples of the unexpected routes taken during the microstructural evolution of pulsed-laser deposited (PLD) free-standing face-centered cubic (FCC) thin films as a function of deposition condition and annealing temperatures. A direct comparison between the grain growth dynamics observed during *in situ* TEM annealing experiments in PLD films of high-purity aluminum, copper, gold and nickel films, as well as aluminum-alumina alloys shows a multitude of kinetics. For high-purity systems film thickness, void density, grain size distribution, and deposition temperature were found to be the primary factors observed controlling the rate, extent, and nature of the grain growth. The growth dynamics ranged from nearly classical normal grain growth to abnormal grain growth resulting in a bimodal grain size distribution. The grain growth rate was found to be highly dependent on the materials system despite all of the films being nanograined FCC metals produced by similar PLD parameters. The investigation of the aluminum-alumina alloys produced under various compositions and deposition parameters suggests that particle pinning can be used to maintain nanostructured films, even after annealing treatments at high homologous temperatures.

In addition to investigating the grain growth dynamics and the resulting grain size distribution, the variety of internal microstructures formed from thermal annealing were evaluated. These structures ranged from intergranular voids to stacking-fault tetrahedra. An unexpected, metastable hexagonal-closed packed phase was indentified in the high-purity nickel films. These *in situ* TEM observations have provided key insight into the microstructural evolution of nanograined free-standing metal films and the defect structure present in the grains resulting from various growth dynamics, in addition to suggesting multiple methods to tailor the structure and the resulting properties of nanostructured free-standing films.

10:40am IS+AS+NS+MI-WeM9 In Situ TEM Studies of Nanomagnetism and Thermal Transport, *J. Cumings*, University of Maryland **INVITED**

The transmission electron microscope is a powerful tool for many areas of nanoscience. The combination of high spatial resolution and high time resolution, giving video-rate imaging, makes it uniquely capable of many types of studies of phenomena in-situ during imaging. Here I will present two areas where we have made recent advances. In nanomagnetic structures, it is possible to image in real-time the reversal process of coupled systems called artificial spin ice. These systems exhibit frustration, leaving disorder in their lowest energy magnetic configurations. I will present studies showing the magnetic reversal processes for these structures, revealing that microscopically correlated events lead to avalanche phenomena. A second topic that I will present is electron thermal microscopy of carbon nanotubes. Here, a new technique will be introduced that allows thermal imaging with nanoscale spatial resolution. This technique has been used to study the thermal transport through carbon nanotubes, and I will present results showing that thermal contact resistance can limit the thermal transport in nanotubes. I will show that this contact resistance can be tuned by two orders of magnitude by appropriately controlling the fabrication of the contacts. Together these results serve to demonstrate the capabilities of studies utilizing in-situ transmission electron microscopy.

11:20am IS+AS+NS+MI-WeM11 In-situ Infrared Transmission Analysis of Atomic Layer Deposition Reactions on Polymer Films and Fibers, *G.N. Parsons, B. Gong, J.S. Jur, C. Oldham, K. Lee*, North Carolina State University

Many new product applications related to packaging, filtration, protection and others offer substantial opportunities and raise new demands for polymer/inorganic thin film integration and surface modification. In-situ transmission infrared spectroscopy can provide critical insight into reaction mechanisms that proceed during inorganic film deposition on organics. We are particularly interested in low-temperature atomic layer deposition (ALD) which ideally proceeds through a binary sequence of self-limiting surface reactions to form highly conformal and uniform films on high surface area structures. In-situ IR spectroscopy allows us to probe and identify specific polymer/precursor reaction mechanisms that occur during precursor and reactant exposure. Typical atomic layer deposition precursors and reactants include trimethylaluminum (TMA), diethyl zinc (DEZ) and water, and polymer materials studied to date include polypropylene, polyamide-6, polyesters (such as polybutylene terephthalate), cellulose, polyvinyl alcohol and others. We have investigated deposition reactions on planar polymer sheets as well as micro- and nano-scale polymer fibers.

In-situ IR transmission data demonstrates that typical non-reactive materials such as polypropylene will take up precursors with minimal precursor/polymer reaction, resulting in subsurface alumina nucleation. Polymers with more reactive backbone or side chain groups, such as cellulose, polyvinyl alcohol or polyamide-6 react readily with the precursor. For example, when polyamide-6 is exposed to TMA, N-H and C-O stretching modes decrease markedly, indicating that TMA attacks the electrophilic carbon atom in the carbonyl group leading to methyl insertion and formation of C-O-Al- and C-CH$_3$ bonds. Electron micrograph images of polyamide fibers after TMA exposure confirms significant extent of reaction. Deposition on cellulose cotton fibers, however, shows primarily surface adsorption, resulting in true ALD growth and highly conformal film coatings by TEM. We will show details of the in-situ transmission ALD reactor, and illustrate how the tool is especially amenable and adaptable to in-situ surface reaction analysis on polymer fiber networks.

Nanometer-scale Science and Technology
Room: La Cienega - Session NS+AS+MN-WeM

Characterization and Imaging at Nanoscale
Moderator: E.I. Altman, Yale University

8:20am NS+AS+MN-WeM2 Surface Preparation of Supported Flat Gold Nanoparticles for use as Au(111) Single Crystal Substrates, *D.H. Dahanayaka, L.A. Bumm*, The University of Oklahoma

Flat gold nanoparticles (FGNPs) grown in aqueous solution have large Au(111) facets that are excellent substrates for scanning probe microscopy. However adsorbed stabilizers (e.g. polyelectrolytes) must be removed or displaced before the FGNP surfaces can be used as single crystal surfaces. We have explored the effects of plasma cleaning, UV ozone, and thermal annealing on the surface roughness and the Au(111) terrace structure using STM.

8:40am NS+AS+MN-WeM3 Determination of the Adsorption Site for Alkanethiol Monolayers on Au(111), *Q. GUuo*, University of Birmingham, UK

The bonding sites for Au-adatom-octanethiolate within the ($\sqrt{3} \times \sqrt{3}$)R30° structure on Au(111) has been investigated with high-resolution scanning tunneling microscopy (STM) imaging. By establishing the relationship between the lateral positions of adsorbates on the top layer of gold and those inside an etch pit, we are able to determine the adsorption configuration with a high degree of accuracy for the illusive ($\sqrt{3} \times \sqrt{3}$)R30° molecular layer. Within any one particular domain, the Au-adatom-octanethiolate species are found to occupy either the fcc hollow or the hcp hollow site.

9:00am NS+AS+MN-WeM4 Atomic Co Wires: Room and Low Temperature STM/STS Measurements, *N. Zaki*, Columbia University, *D. Acharya*, Brookhaven National Laboratory, *D.V. Potapenko*, Columbia University, *P. Johnson, P. Sutter*, Brookhaven National Laboratory, *R.M. Osgood*, Columbia University

9:20am NS+AS+MN-WeM5 Atomic-Resolution Spin Mapping by Exploiting Magnetic Exchange Forces, *R. Wiesendanger**, University of Hamburg, Germany **INVITED**
While Spin-Polarized Scanning Tunnelling Microscopy (SP-STM) [1] is nowadays well established for revealing atomic spin configurations at surfaces, its application is limited to electrically conducting samples such as magnetic metals or semiconductors. In order to map atomic spin structures at surfaces of insulators and to open up the exciting possibility of studying spin ordering effects with atomic resolution while going through a metal-insulator transition, we have developed Magnetic Exchange Force Microscopy (MExFM) [2]. This technique is based on the detection of short-range spin-dependent exchange and correlation forces at very small tip-sample separations (a few Angstroms), in contrast to Magnetic Force Microscopy (MFM) where the magnetic dipole forces are probed with a ferromagnetic probe tip at a typical tip-to-surface distance of 10-20 nm [3]. MExFM has allowed a first direct real-space observation of spin structures at surfaces of antiferromagnetic bulk insulators [2] as well as ultrathin films [4]. Moreover, it provides a powerful new tool to investigate different types of spin-spin interactions based on direct-, super-, or RKKY-type exchange down to the atomic level. By combining MExFM with high-precision measurements of damping forces [5] localized or confined spin excitations in magnetic systems of reduced dimensions become experimentally accessible [1].

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M. Ashino, R. Wiesendanger, A. N. Khlobystov, S. Berber, and D. Tomanek,

Phys. Rev. Lett. **102**, 195503 (2009)

10:40am NS+AS+MN-WeM9 Chemical Imaging and Interaction Quantification on the Surface Oxide Layer of Cu(100) Using High-Resolution Atomic Force Microscopy, *M.Z. Baykara, T.C. Schwendemann, H. Mönig*, Yale University, *M. Todorovic, R. Pérez*, Universidad Autónoma de Madrid, Spain, *E.I. Altman, U.D. Schwarz*, Yale University
Chemistry is governed by the interactions between atoms and molecules. On surfaces, chemical forces extending into the vacuum direct the behavior of many scientifically and technically important phenomena including surface catalysis. Therefore, it would be useful to map and quantify the interactions between a catalytically active surface and a probe with atomic resolution in order to study the role and effectiveness of various surface defects such as vacancies, impurities, steps, kinks, and domain boundaries as active sites. An ability to discriminate between different chemical species on the sample surface would offer further insight. In this talk, we will show with the example of an oxygen-reconstructed copper (100) surface that much of this information can be derived from combining the new method of three-dimensional atomic force microscopy (3D-AFM) [1], a variant of noncontact atomic force microscopy, with scanning tunneling microscopy. The surface oxide layer of Cu(100) features domain boundaries and a distinct structure of the Cu and O sublattices that is ideally suited for such model investigations. While different tips show different chemical contrasts, 3D data sets enable site-specific quantification of force interactions and tunneling currents. In order to clarify the different contrast modes data, DFT total-energy calculations and Non-equilibrium Green's Function (NEGF) methods for electronic transport have been used to determine the interaction and the tunneling current [2-4] for a large set of tip models. These calculations provide insight into (1) the fundamentals of contrast formation in this experimental technique and (2) into the correlation between tip-sample forces and local chemical reactivity, factors that are essential for the further development and application of this novel approach to characterizing catalytic activity.

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11:00am NS+AS+MN-WeM10 Comparison of Resonant-Frequency Techniques for AFM Nanomechanical Mapping, *D.C. Hurley, J.P. Killgore, A.B. Kos*, NIST, *A. Gannepalli, R. Proksch*, Asylum Research
Contact-resonance force microscopy (CR-FM) is an emerging AFM technique for quantitative imaging of near-surface nanoscale mechanical properties. In CR-FM, the resonant frequency f of the cantilever is measured when the tip is in contact with the sample. Mechanical-property values are obtained from the frequency data with the use of models for the vibrating cantilever and the tip-sample contact. Contact-resonance measurements were originally made at a fixed sample position with off-the-shelf electronics. However, to achieve sufficient speed for CR-FM imaging, it has been necessary to develop new instrumentation approaches. Here we describe work to directly compare three methods for CR-FM imaging: the SPRITE (Scanned Probe Resonance Image Tracking Electronics) approach developed at NIST, the DART (Dual AC Resonance Tracking) approach developed by Asylum Research, and the BE (Band Excitation) method originally developed at Oak Ridge National Laboratory and implemented by Asylum Research. Each method enables contact-resonance frequency mapping but achieves it through different practical implementations. First, we will discuss the concepts on which each method is based. Next, results of comparison experiments will be presented in which images were acquired with each method in succession on the same AFM instrument. A variety of specimens were imaged to probe the strengths and limitations of each method. For example, we found that DART could operate at higher scan speeds, while SPRITE and BE were better able to track very asymmetric peaks that presumably originate from nonlinear tip-sample interactions. Both DART and BE provide values of the resonance quality factor Q in addition to the resonant frequency f, while currently SPRITE measures f only. Despite these differences, the methods yielded similar results in many cases. The availability of a broader array of frequency mapping tools will ultimately facilitate the widespread application of CR-FM to nanoscale materials science.

11:20am NS+AS+MN-WeM11 Single Molecule Structural Transitions of Water Polymer Chains in a Nanoscale Confined Space Studied by COIFM, *B.I. Kim*, Boise State University
Interfacial water structures have been investigated in an ambient environment between two silica surfaces using a newly developed cantilever based optical interfacial force microscope (COIFM). As the gap distance decreases between the tip and the substrate, a remarkable oscillatory behavior is oberved in normal and friction forces. Our further analysis suggests that water molecules confined between tip and substrate in an ambient environment form a bundle of water chains through hydrogen bonding. Each chain length is analyzed by a model called "freely jointed chain" (FJC) model in which the individual segments can rotate freely. The bundle of water chains experiences multiple layering transitions (without single layer transition) from $l = 36$ diameters to $l=12$ diameters as the tip approaches the surface. The analysis shows that the number of links (l) decreases by 5,4,3,3,3,3,4,5 in water diameters. The result indicates that, as the gap between the tip and the substrate decreases, the interfacial water molecules favor multilayer transitions to stepwise, single layer transitions. The multilayer transitions consist of a sequential reduction of total chain length by integer number of water diameters. The loss of one water diameter in overall chain length represents a highly cooperative transition, whereas the loss of two additional water diameter along the sigmoidal shape is reminiscent of a well-known two state transition. As a model to describe these transitions, a kink is introduced in the chain by rotating one water molecule 90 degrees while maintaining the number of hydrogen bonds in the chain. The other remaining molecules still follow the freely jointed chain model.

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* NSTD Recognition Award

Applied Surface Science
Room: Cochiti - Session AS-WeA

Surface Mass Spectrometry: SIMS and Beyond
Moderator: C. Szakal, National Institute of Standards and Technology

2:00pm AS-WeA1 Exploring the Surface Sensitivity of ToF-SIMS: Measuring the Implantation Depths and Sampling Depths of Bi_n and C_{60} Ion Sources in Organic Films, *S. Muramoto, J. Brison, D.G. Castner*, University of Washington

When a pulsed Bi_n^+ analysis beam and a direct current C_{60} etching beam are used in ToF-SIMS dual-beam depth profiling, we observed that increasing the ion dose of the analysis beam decreased the molecular signal as a function of depth. This decay was seen to occur much earlier in the depth profile for less clustered ions, suggesting that damage is related to the implantation depth of the primary ion. Recent experimental and simulation results in this field indicate that implantation depth is inversely related to the clustering of the primary ion, and are observed to affect outcomes such as sputter yield and escape depth (sampling depth). There is a need to characterize these parameters on organic systems, since a better understanding of these parameters will help us choose experimental parameters for the optimal analysis of samples.

In this study, the above mentioned quantities for Bi_n^{q+} (n = 1, 3, 5, q = 1, 2) and C_{60}^{++} ions were characterized on molecular and polymeric organic films; a spin-cast trehalose and a plasma polymerized tetraglyme, both about 100 nm thick. The implantation depths of Bi ions were determined using C_{60} single-beam depth profiling of the same area bombarded by bismuth. The depth scale was calibrated using AFM. The sputter yield was obtained by AFM imaging of the sputter crater. The molecular escape depth was determined by capping a protein-adsorbed mica with tetraglyme overlayers of varying thicknesses and monitoring the protein fragment intensities as a function of thickness. Results show that an ion's penetration depth is directly proportional to the energy-per-constituent of the ion. For example, increasing the number of Bi atoms from 1 to 3 (Bi_1^+ to Bi_3^+) for 25 keV single charged ions decreased the average penetration depth from 18 to 10 nm. When the energy of Bi_3 was increased from 25 to 50 keV, the implantation depth increased from 10 to 14 nm. When implanting bismuth ions, we observed etching of the sample surface, with the crater depths proportional to the cluster size of the bismuth ion. These crater depths were also proportional to the escape depth of the protein fragments. Bi_1^+ at 25 keV was found to be the most surface sensitive; its sampling depth was only 1.8 nm despite its implantation of 18 nm. The second most surface sensitive was C_{60}^{++} at 20 keV with a molecular escape depth of 2.4 nm. It turned out that the single most important factor that determined the surface sensitivity of the ion source was its sputter depth; both Bi_1^+ and C_{60}^{++} eroded 0.3 and 1.0 nm, respectively, whereas Bi_5^{++} with a sputter depth of 1.8 nm was the least surface sensitive with a molecular escape depth of 4.7 nm.

2:20pm AS-WeA2 A New Cluster Ion Beam for Advanced Molecular Depth Profiling of Polymers by TOF-SIMS, *T. Miyayama, S. Iida, N. Sanada, M. Suzuki,* ULVAC-PHI, Japan, *G.L. Fisher, J.S. Hammond, **S.R. Bryan***, Physical Electronics

The introduction of C_{60}^+ as a sputter beam for TOF-SIMS made it possible to acquire molecular depth profiles on a wide variety of polymers. Previous studies by many different groups have demonstrated that not all polymers can be successfully depth profiled and that certain classes of polymers undergo sputter-induced chemical reduction when bombarded by C_{60}^+ ions. If the polymer sputter yield is not high enough, the subsurface sputter-induced damage will accumulate as a function of sputter ion dose and the secondary molecular ion signals will not be stable. A number of different analytical parameters have been previously explored in attempts to improve depth profiling of these difficult polymers including sample temperature, beam energy, and incidence angle. We reported last year that glancing C_{60}^+ incidence angle (76° from surface normal) significantly improved the ability to depth profile polycarbonate and polystyrene, which were previously unsuccessful at a typical incidence angle of 48°. However, even under these optimized conditions, the depth profiles eventually fail after several hundred nanometers due to accumulated sputter damage to the polymer and a concurrent reduction of the secondary ion and sputter yields. In the present study, we report the efficacy of an argon gas cluster ion beam (GCIB) for steady-state molecular depth profiling the same polymer systems. Depth profiles using different GCIB experimental conditions will be reported and compared to C_{60}^+ depth profiles acquired under optimized conditions.

2:40pm AS-WeA3 Nanoparticle Surface Analysis by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Low Energy Ion Scattering (LEIS), *T. Grehl, P. Bruener, E. Niehuis,* ION-TOF GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *R. ter Veen, M. Fartmann, D. Breitenstein*, Tascon GmbH, Germany

Due to their extraordinary properties nanoparticles enter more and more fields of industrial production and daily life. They facilitate the protecting effect of sun creams, make car coatings and spectacle lenses scratch resistant and reliably protect shoes from wetness. Nanoparticles with antibacterial properties are used in clothing and refrigerators.

Nanoparticles' properties are influenced by their high surface to volume ratio. In addition, specifically tailored nanoparticles are increasingly composed of core shell structures. In order to understand and further develop the properties of nanoparticles it is therefore important to develop tools to investigate the elemental and molecular composition of their surfaces and interfaces.

Two ion beam technologies show promising features in this respect: On the one hand Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is able to probe the outermost 3-5 atomic layers of a sample. It reveals the elemental as well as the molecular composition of the samples' surface in a semi-quantitative manner. On the other hand, Low Energy Ion Scattering (LEIS) is a quantitative technique to probe the elemental composition of the outermost atomic layer. Combining these two complementary techniques allows a comprehensive overview on the sample composition.

In our study we will present combined ToF-SIMS and LEIS data on model-nanoparticle systems and will give examples for their prospects to enable nanoparticle development, product control and failure analysis. Amongst others, the layer growth of a shell of Al_2O_3 on $LiMn_2O_4$ nanoparticles deposited by an ALD process was investigated. Both techniques are able to determine the increased coverage of the core. While ToF-SIMS yields additional information about organic residues, LEIS is able to quantify the surface composition and assess the integrity of the layer.

3:00pm AS-WeA4 Dual Beam Depth Profiling of Organic Materials by Time-of-Flight Secondary Ion Mass Spectrometry under Optimized Ion Beam Conditions, *D. Rading, R. Moellers, F. Kollmer, T. Grehl,* ION-TOF GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *E. Niehuis*, ION-TOF GmbH, Germany

In recent years the development of sputter depth profiling of organic materials using Time of Flight instruments has made rapid progress. In particular, the use of a high energy C60 cluster ion beam for sputtering has drawn considerable interest [1-3]. However, it has also been demonstrated that a variety of organic compounds cannot be profiled in a satisfactory way as characteristic molecular secondary ion signals are lost under high dose cluster ion bombardment [4-6]. In a number of studies various approaches were applied in order to overcome this problem. These approaches included sputtering at low incident angles [7], sputtering with low energy Cs ions [8], cooling or heating of the sample [5,9,10] and using alternative cluster ion sources such as massive argon clusters [11]. As a suitable sample for more detailed studies on properties, such as depth resolution was not available, most of the work so far was of phenomenological kind, i.e. it was checked whether characteristic organic signals survived the sputter process.

In this contribution, we investigate the influence of sputtering and analysis beam conditions on the signal intensity of characteristic high-mass molecular ions under high primary ion flux. For this purpose a series of primary ion species (C60, Bin, Cs) at various energies and angles has been applied. In a second step an Irganox multilayer sample introduced by NPL [10] was used to investigate the influence of energy and angle of a C60 sputter beam as well as the influence of sample rotation on depth resolution, constancy of the sputter rate and quantification possibilities in organic depth profiling.

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4:00pm AS-WeA7 Fundamental Sputtering Yields of Nanoparticles using SIMS, *J.L.S. Lee*, I.S. Gilmore, D.C. Cox, M.P. Seah, S.J. Spencer, National Physical Laboratory, UK

Nanoparticles are front-runner nanotechnologies key to high innovation products, such as biodiagnostics, drug delivery, medical imaging (contrast agents), cosmetics, sunscreens and catalysts. The surface and bulk chemistries of nanoparticles are crucial for their unique properties. There is also increasing concern over the potential health, environmental and safety risks of nanomaterials. Robust and consistent methodologies for characterising nanoparticle surface and bulk chemistries are urgently needed to support standardisation, regulatory requirements and toxicology studies [1].

Secondary ion mass spectrometry (SIMS) has been applied in nanoparticle characterisation [2,3]. However, the fundamentals of the sputtering of nanoparticles are not yet well understood. The sputtering yield is expected to be significantly different for nanoparticles compared to bulk materials, due to the dimension of nanoparticles being similar to the size of the SIMS collision cascade, and the larger available surface area for secondary emission. In this study, SIMS depth profiles were obtained for model Au nanoparticles, with diameters ranging from 10 nm – 100 nm, dispersed and mounted onto a silanised silicon substrate. The sputtering yields and profile shapes are evaluated for both atomic and cluster primary ion beams (Ar^+, Bi^+, Bi_3^+ and C_{60}^{n+}), using a range of primary ion energies. The nanoparticles are characterised by SEM and AFM both before and after sputtering. There is a significant increase in the sputtering yield for nanoparticles compared with bulk materials, in agreement with predictions from a recent molecular dynamics study [4]. In addition, for the first time, we observed the sputtering of nanoparticles in real time using a focused ion beam system with simultaneous SEM imaging. This provides valuable information for interpreting the SIMS depth profiles of nanoparticles and an interesting phenomenon of nanoparticle coalescence was observed. These results contribute towards developing the essential underpinning metrology and providing a practical procedure to analysts for the chemical characterisation and compositional depth profiling of nanoparticles.

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4:20pm AS-WeA8 SIMS: Cluster Primary Ion Sputtering - Practical Reference Data and Outlook for High-Resolution Organic Imaging, *I.S. Gilmore*, T.L. Salter, J.L.S. Lee, F.M. Green, M.P. Seah, National Physical Laboratory, UK

Cluster ions have become the ion beam of choice for the analysis of organics in ToF-SIMS, owing to the large enhancement of the molecular ion yield [1] and the ability to depth profile through certain organic materials [2,3]. However, there is currently a lack of practical reference data on the sputtering yield volumes and damage cross-sections for commonly encountered materials in industry. Aside from having fundamental importance, these data can aid analysis by informing optimal analysis parameters, such as the useful lateral resolution achievable [4]. In this work, a systematic study using Bi+, Bi3+, Bi5+ and C60+ ions is conducted for industrially relevant organics (PMMA, PVP, hydroxypropyl cellulose, phenylalanine, cholesterol, rhodamine and Irganox 1010). We provide general recommendations to help analysts.

For some organic materials thicker than a monolayer, the traditional static SIMS limit may be exceeded since the secondary ion intensity is retained as the material is consumed. The useful lateral resolution may therefore be improved by integrating intensity. However, the ultimate lateral resolution is also limited by the ion source brightness. The reference data here and ion source design constraints define the present frontier of SIMS in terms of spatial resolution and molecular information. We show how this frontier has moved forward dramatically over the last 10 years and what barriers need to be overcome to allow nanoscale molecular imaging in SIMS.

References

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4:40pm AS-WeA9 Sample Preparation of Cellular Samples for ToF-SIMS Analysis, *M.A. Robinson*, D.G. Castner, University of Washington

Over the last decade time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been increasingly used for examining (imaging) biological samples ranging from surface immobilized proteins to tissue sections to single cells. Due to the ultra high vacuum requirement of the ToF-SIMS technique careful and stringent sample preparation protocols are necessary to preserve the native state of these samples. There are a variety of preparation procedures that have been developed to address this need. However, there is still debate as to which procedure best preserves cell chemistry and morphology. The goal of this study is to further elucidate the differences in information that can be obtained when comparing cellular samples that have been plunge cooled and then freeze dried versus those that have been plunge cooled and analyzed in the frozen hydrated state.

Freeze drying biological samples after cryofixation is a much simpler method of sample preparation compared to frozen hydrated. We have shown that freeze drying cryofixed samples preserves the native morphology as well as the K^+/Na^+ gradient in single NIH 3T3 fibroblasts, as shown in Figures 1a and 1b. Given optimal preparation procedures, images of subcellular compartments can be realized, as seen in Figure 1c. A single cell is shown after C_{60}^{++} sputtering (C_{60}^{++} ion dose = 4.3×10^{14} ions/cm^2). The nucleus can be seen in the circular area within the cell that lacks $C_3H_8N^+$ signal. A nucleolus is observed as the bright spot within the nucleus. Also noticeable is the $C_3H_8N^+$ signal is the Golgi apparatus in the perinuclear region.

The question that remains is what type of information can be obtained from samples that have been freeze dried? Some groups have reported that freeze drying will cause cellular damage [1], while others have reported detrimental effects from frozen hydrated analysis [2]. Freeze drying continues to be the most popular preparation method after cryofixation, most likely because it is less complex than frozen hydrated analysis, as well as the fact that few ToF-SIMS instruments are setup to easily perform this type of investigation. We are adapting a liquid nitrogen cooled sample stage to allow for the rapid entry of cellular samples at liquid nitrogen temperatures to avoid sample warming and ice crystal formation. Ice crystal formation must be avoided in frozen hydrated analysis of biological material, as ice crystal formation will rupture cell membranes causing a loss of morphological and chemical information.

The results from this study shows the differences in information obtained when analyzing similar cellular samples in the freeze dried state versus the frozen hydrated state.

5:00pm AS-WeA10 "Wet SIMS": A Novel Molecular Imaging Technique for Biological Material Analysis, *J. Matsuo*, Kyoto University, CREST, Japan, *H. Yamada, Y. Wakamatsu,* Kyoto University, Japan, *T. Aoki, T. Seki*, Kyoto University, CREST, Japan

Because of the complexity of the structure and chemical composition in living organisms, much progress has been made in realizing mass imaging for biological samples. Secondary ion mass spectrometry (SIMS) imaging technique has the significant advantage of high spatial resolution, free of matrix deposition and with good reproducibility. In conventional SIMS the primary probes are keV-energy ion beams, which deposit their energy to atomic nuclei. As a result, primary ions break molecular bonding, and molecular information is lost. On the other hand, MeV-energy ions enhance ionization of high mass molecules, because of their dense electronic excitation. Molecular images with lateral resolution of around 5 mm have been demonstrated for peptides or lipids using MeV-energy ion beams [1].

In addition, MeV-energy ions, which have a long projection range in matter, can be utilized for material analysis under low vacuum. The low-vacuum condition prevents evaporation of water from the biological sample and helps maintain the shape of the sample. A new instrument has been developed to realize SIMS measurements under low vacuum. Biological samples were analyzed with swift heavy ions, and secondary molecular ions

were introduced into a quadrupole ion guide combined with a differential pumping system. An orthogonal time-of-flight (o-ToF) retaining high vacuum was employed to measure secondary ion mass spectra. This system allows the use of continuous beam, because of collisional cooling and orthogonal extraction. The mass resolution of this system is better than 6000, and is independent on the primary beam. Molecular imaging of cells and tissues was observed with a sample-scanning system. Secondary emitted biomolecular ions, such as lipids or cholesterols, were clearly observed with sufficiently high intensity. This new technique opens new possibilities for SIMS analysis, and we called it "wet SIMS".

Recent progress in this novel technique will be presented and discussed in view of its possible application in the analysis of biological matter.

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5:20pm AS-WeA11 Improvement of Organic Ion Yields in Secondary Ion Mass Spectrometry via Water Vapor Injection, *T. Mouhib*, *A. Delcorte, C. Poleunis, P. Bertrand*, Université Catholique de Louvain, Belgium

Even though significant progress has been achieved in molecular characterization by secondary ion mass spectrometry (SIMS) of organic compounds, some challenges still exist. One important limitation concerns the sensitivity the technique, often insufficient for high resolution molecular imaging. Several approaches have been proposed to increase the useful molecular signal intensities. The first one involves specific sample preparation procedures, such as the use of special matrices or metal-assisted SIMS (MetA-SIMS), in which metal nanoparticles are condensed on the sample surface. The second type of improvement directly involves the choice of the projectile, i.e. atomic projectiles are replaced by clusters, such as Au_n^+, Bi_n^+, C_{60}^+ and SF_5^+.

In this contribution, we investigate a new protocol to improve the analytical performance in organic SIMS, using water vapor injection at relatively high pressure near the sample surface. A significant enhancement of the positive secondary ion intensities is observed for organic materials irradiated with 12 keV Ga^+ ions in the presence of H_2O gas. In addition, our results show that the enhancement depends on the type of secondary ion and that the formation of protonated ions is specifically favored. For the low molecular weight additive Irgafos 168 ($C_{42}H_{63}O_3P$), the normalized $[M+H]^+$ intensity increases by more than 50 times upon H_2O flooding. The enhancement factors are lower with high molecular weight polymers. Nevertheless, the intensity of the protonated monomer ions is also enhanced preferentially in comparison with those of the deprotonated and the bare monomer ions. In the next phase of this work, we consider the combination of H_2O vapor flooding with polyatomic projectile bombardment.

5:40pm AS-WeA12 IonCCD^{TM} for Charged Particle Detection: From sub-keV Electrons and keV Atomic and Molecular Ions to Hyperthermal Biomolecular Ions, *O. Hadjar*, OI Analytical, *W.C. Schnute*, Dionex Corporation, *J. Laskin*, Pacific Northwest National Laboratory

We will present the latest data using a pixel array for charged-particle detection based on a modified charge-coupled device technology (IonCCD^{TM}). The array is 51 mm long, consists of 2126 pixels (1.5 mm long) with 0.024 mm pitch. The charged particle beam is collected individually by each pixel, and hence, the IonCCD signal response is proportional to the beam flux and the collection time (integration time). With an integration time of 82 μs and a readout time of 2.7 ms, the IonCCD produces 360 frames a second. We will present data showing the direct use of the IonCCD as a beam profiler (one dimensional) to characterize the positively and negatively charged ion beams exiting an RF-only collisional quadrupole. The latter is used to thermalize and collimate the ions produced by an atmospheric pressure electrospray source. When mounted on the focal plane of a miniature Mattauch-Herzog geometry sector-field analyzer, the IonCCD produces a mass-over-charge (m/z) spectrum of the produced ions. For high sensitivity measurements we coupled the IonCCD to a micro-channel plate (MCP). In this manner, the IonCCD is used as an anode to read the electrons produced by the MCP. We will present MCP-IonCCD mass spectra using an electron-impact (EI) source to produce singly and doubly charged Xe ions. We compare the performance of the MCP-IonCCD hybrid detector to that of the IonCCD itself. We will apply this technology to the simultaneous m/z separation and detection of negative ions produced by electrospray ionization that generates beams of deprotonated molecules that are typically 10 times weaker than ion beams produced in the positive mode.

In Situ Microscopy and Spectroscopy Topical Conference
Room: Acoma - Session IS+BI+AS-WeA

In Situ Microscopy/Spectroscopy – Biological Interfaces
Moderator: M. Grunze, University of Heidelberg, Germany

2:00pm IS+BI+AS-WeA1 Adsorption and Phase Transition of Liposomes via Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy, *M.R. Hernandez*, *T.C. Ng, E.N. Towns, B.C. Walsh, D.P. Land*, University of California at Davis

Liposomes are becoming increasingly prevalent as an important part of drug delivery systems in modern medicine, however a better understanding of the physical characteristics is needed. In this study we present our results on the stability and adsorption of liposomes formulated from dipalmitoylphosphatidylcholine (DPPC) via attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. The phase transition temperature of liposome formulations of pure DPPC, DPPC and cholesterol, and DPPC, cholesterol, and 1,2-Distearoyl-phosphatidylethanolamine-methyl-polyethyleneglycol -2000 (DSPE-mPEG2000) is determined using a temperature dependant study (25°C to 50°C) and been found to occur abruptly around 41°C for pure DPPC liposomes and exhibit gradual temperature changes from 35°C to 43°C for the other two liposome formulations. We have studied the adsorption characteristics of different formulations of liposomes with both hydrophobic and hydrophilic surfaces created by different self-assembled monolayers, and will present a new method for studying an in vitro way of studying the adsorption of different formulations of liposomes onto a surface of immobilized proteins. Knowing the stability of liposomes and liposome-protein adsorption characteristics allows for a better understanding of their use and design of future formulations in drug delivery systems.

2:20pm IS+BI+AS-WeA2 Synchrotron Based Infrared Imaging at the Diffraction Limit, *J. Nasse,* University of Wisconsin-Milwaukee, *C. Gohr, A. Rosenthal*, Medical College of Wisconsin, *C. Hirschmugl*, University of Wisconsin-Milwaukee

A new mid-infrared beamline (IRENI) extracting a large horizontal swath of radiation (320 hor. x 25 vert. mrads^2) to homogeneously illuminate a commercial IR microscope equipped with an infrared Focal Plane Array (FPA) detector has recently been commissioned at the Synchrotron Radiation Center in Stoughton, WI. This new facility provides the opportunity to obtain chemical images with diffraction-limited resolution, for all wavelengths in the mid-IR concurrently, in minutes. The design of this facility and an initial application will be presented.

IRENI combines a bright IR synchrotron source to an FTIR microscope with a multi-element detector for wide-field imaging as opposed to the common dual-aperture geometry with raster scanning that is available at most synchrotron IR beamlines. The swath of radiation from the SRC is extracted as 12 beams and recombined into a 3 x 4 bundle of beams that is refocused onto a sample plane of an infrared microscope illuminating 40 x 60 micron^2 sample area. The sampled spatial resolution is defined by both the magnification after the sample and the FPA pixel size. Here, a 74x Schwarzschild objective achieves effective geometric pixel sizes of 0.54 x 0.54 micron^2, which is approximately λ/4 for even the shortest wavelength of 2 μm. This spatial oversampling provides adequate information to obtain concurrent, diffraction-limited images across the entire spectral range. In addition, the spectral quality is excellent, since the high density, stable, broadband flux from the synchrotron achieves high quality spectra for 0.54 x 0.54 micron^2/pixel using similar measuring times as table-top instruments that image 5.5 x 5.5 micron^2/pixel.

The presence of calcium-containing crystals, including calcium pyrophosphate dihydrate (CPPD) and hydroxyapatite-like basic calcium phosphate (BCP), in synovial fluids plays a major role in cartilage degeneration in osteoarthritis. Models of calcium crystal formation tend to produce small, sparse crystals embedded in debris enriched in proteins, lipids, and carbohydrates, which interfere with many identification techniques. Synchrotron FTIR imaging circumvents difficulties in identifying these crystals and also allows for characterization of the surrounding matrix. We present results from well-characterized models of calcium crystal formation that demonstrate our ability to both identify crystals *in vitro* and characterize the matrix surrounding these crystals.

2:40pm IS+BI+AS-WeA3 Proteins and Lipids at Liquid/Solid Interfaces: *In situ* Studies by Neutron Reflectometry and Infrared Spectroscopy, *M. Strobl, M. Kreuzer,* University of Heidelberg, Germany, *M. Reinhardt, R. Steitz,* Helmholtz Zentrum Berlin, Germany, *M. Grunze, R. Dahint*, University of Heidelberg, Germany **INVITED**

4:00pm IS+BI+AS-WeA7 Biological Imaging with Coherent X-rays: The Lens-less Approach to High Resolution, *A. Beerlink*, Universität Göttingen, Germany **INVITED**
Understanding molecular functions in complex environments such as biological cells or novel composite materials are a prerequisite for the advancement of nano and biomedical sciences. They require a combination of high spatial resolution, quantitative contrast and

full compatibility with environmental conditions, such as aequous media. To this end, the potential of x-ray imaging is not yet fully developed, but currently undergoes rapid progress. While classical x-ray microscopy based on Fresnel zone plates has matured and provides useful structural information in a growing range of applications, this technique is severely limited by the nanostructuring process of the lenses. In

recent years, novel lens-less approaches for imaging have emerged, where the object functions are reconstructed from the measured intensities

either in the far-field regime, or under near-field conditions (propagation imaging). We present experiments using x-ray quasi point sources to illuminate the sample in combination with digital recording of the resulting diffraction patterns. One focus is the applicability towards biological samples, for which the imaging properties of the different coherent microscopy approaches will be compared. In this context, recent results obtained with ultrabright femtosecond pulses provided by the free electron laser FLASH will be presented and accessible information complementary to synchrotron imaging will be discussed.

4:40pm IS+BI+AS-WeA9 Dielectric Constant and Polarization of Biomolecules Determined by Torsional Resonance Nanoimpedance Microscopy, *K. Kathan-Galipeau, S.U. Nanayakkara, P.A. O'Brien, B.M. Discher, D.A. Bonnell*, University of Pennsylvania
We have developed a new technique, torsional resonance nanoimpedance microscopy (TR-NIM), that allows for the measurement of frequency-dependent local transport properties on soft materials. AFM measurements at torsional resonances provide a key advantage: the ability to achieve low-force scanning while maintaining the tip in the near-field. As a result, it is possible to measure impedance between the tip and sample without damaging the sample.

This technique has been used to determine the resistance, capacitance, and dielectric properties of a novel class of biomolecules. These redox active molecules, known as maquettes, consist of dimers and tetramers of alpha helix polypeptides and provide a convenient functional alternative to natural proteins. Maquettes are capable of binding a range of cofactors; this study examines the properties of iron and zinc porphyrins. Maquettes serve as a benchmark for integrating electronics with biologically inspired materials that possess unique characteristics, such as electron-transfer capability, the possibility of gating redox activity, optoelectronic functionality, and nanometer size.

In order to determine the behavior of these functional biomolecules on electrodes, PDMS stamping was used to create stripes that alternate between maquettes and bare graphite. Stamping also allowed us to control the assembly of the redox-active maquettes from multilayers to horizontally oriented monolayers (maquettes laying down) and vertically oriented monolayers (maquettes standing up) by varying the stamping time and the concentration of the maquettes in organic solvents.

Interestingly, we observe that the resistance decreases with increased height of maquettes, which is explained in terms of the configurations of the molecules on the electrode. The dependence of local impedance on exposure to optical radiation revealed an increase in capacitance and decrease in resistance when the maquettes are exposed to 425 nm light. This is true for both zinc and iron porphyrin cofactors. We attribute the decrease in resistance to photoactivated current. The increase in capacitance is due to an increase in the polarizibility of the maquettes.

5:00pm IS+BI+AS-WeA10 Dynamic Observation of Phospholipid Model Cell Membranes and Particles by STM and Vibrational Spectroscopy, *T. Yamada*, RIKEN, Japan, *S. Matsunaga,* The University of Tokyo, Japan, *T. Kobayashi,* RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan
Scanning tunneling microscopy (STM) and other surface-scientific techniques can be utilized to explore the microscopic dynamics of biological molecules in the context that the techniques are applicable for solid surfaces immersed in aqueous solutions. We devised STM and vibrational spectroscopies to make usable for molecular monolayers at

solid-liquid interface. We attempted to observe phospholipid layers formed on octanethiol-terminated gold (111) single-crystalline substrates placed in aqueous buffer solutions (in situ STM). By in situ STM we could observe dihexanoyl-*sn*-glycero-3-phosphocholine (DHPC), a relatively short kind of lipid, forming a fluidic monolayer. A crystalline phase of this monolayer was observed by applying an electrode potential compatible with the membrane potentials of real cells. Furthermore, mixed lipid layers have been examined by STM [1]. We found some nanometer-scale raft structures (phase-separated domains), which are functionally characteristic for real cell membranes. We also studied phospholipid particles suspended in buffer solutions. Suspensions were prepared from a phosphcholine (PC) and an ethanolamine (PE), consisting of nanometer-scale phospholipid particles with narrow size distribution. In situ STM revealed particles with a diameter ~ 10 nm (named "minimal lipid particles (MLP)"), forming a monolayer along the Au(111). It is known that some categories of antibiotics selectively attack lipids contained in germ cell membranes and disintegrate the whole cells. We chose "duramycin", a 19-residued peptide antibiotic, which specifically binds PE. When the total concentration of phospholipid was controlled between 100 μM and 500 μM, a layer of MLP was discerned. During STM scanning, 7 μM of duramycin solution was added into the suspension, and the PC+PE MLP became fragile and seemed to be scratched by the tip, ending up with a widespread multilayer. This sort of highly leveraged effect of duramycin is characteristic in the action of antibiotics [2]. These works demonstrated the advantage of STM in monitoring the live nanometer-scale reactions of biological entities, which have not been recognized experimentally so far. We expect more application of STM in physiological investigation in cell biology.

[1] S. Matsunaga et al., *Electrochem. Commn*. **9** (2007) 645.

[2] S. Matsunaga et al., *Langmuir* **25** (2009) 8200.

5:20pm IS+BI+AS-WeA11 Rapid In-Situ Assessment for Microbes on Simultaneously Prepared Plate with Substrate and Zirconium Based Thin Film Metallic Glasses (TFMGs), *P.T. Chiang*, I-Shou Univ./Fooyin Univ. Hospital, Taiwan, Republic of China, *G.J. Chen, H.H. Liu, Y.H. Shih*, I-Shou Univ., Taiwan, Republic of China, *J.P. Chu*, National Taiwan Univ. of Science and Technology, Taiwan, Republic of China, *J.S.C. Jang*, National Central Univ., Taiwan, Republic of China
ZrAlNiCuSi TFMGs could modify the stainless steel's surface with high hardness, scratch-adhesion capabilities. Zr-based TFMGs' smooth surface could decrease and prolong the lag phase of microbes' growth for at least 24 hours.

The actual numbers of pathogenic bacteria might be underestimated by conventional methods due to sublethal injury, malnutrient's and other physiological factors which reduce bacterial viability. Moreover, these methods would limit the real-time quantitative detection and easily cause contaminations with bias.

Rapid comparisons in the same culture condition are obtained on a simultaneously prepared plate with substrate and Zr based TFMGs. By utilization of GFP plasmid (pGLO) into HB101 with 10mM arabinose induction, we could measure the intensity of green fluorescence by LAS-3000 fluorescent detector to setup the real-time monitor system for observation of bacterial growth on TFMGs' surface.

This integrated method was time-saving, cost-effective and simple. The serially rapid in situ monitor of the microbial growth will emerge as a novel tool to realize the TFMGs or other materials' antimicrobial properties.

Thursday Morning, October 21, 2010

Applied Surface Science
Room: Cochiti - Session AS1-ThM

Advanced Automation and Data Processing
Moderator: V. Smentkowski, GE Global Research Center

8:20am **AS1-ThM2 Chemical State Thin Film Characterisation by Angle Resolved XPS Using the Maximum Entropy Method**, *A.J. Roberts, G. Mishra, K. Macak,* Kratos Analytical Ltd., UK, *C. Moffitt,* Kratos Analytical Inc., UK

The application of thin films with nanometre thickness is being driven by their use in many industries. Angle resolved x-ray photoelectron spectroscopy (ARXPS) is a uniquely placed technique providing non-destructive quantitative chemical state depth distribution of elements in the first few nanometres of a surface.

Acquisition of ARXPS using modern instrumentation is now straight forward but determining the depth distribution of elements and their chemistry is more challenging. One numerical method for the reconstruction of depth profile data from ARXPS is the maximum entropy method (MEM). The precision of the reconstructed depth profile depends both on the noise in the experimental data and on the accuracy of the physical model. Furthermore effects of elastic scattering of the photoelectrons and analyser acceptance angle of the analyser must also be adequately accounted for. The influence of the fitting algorithm on reconstructed depth profiles from ARXPS has recently been reviewed [1] for high-k multilayer materials with emphasis on the importance of prior knowledge and/or constraints to achieve high quality profiles. Work presented here expands on the previous conclusions and explores the effect of data collection conditions such as instrument operating mode, analyser collection angle and signal to noise on the reliability of reconstructed profiles for multilayer thin films and modified surfaces.

[1] T. Conard, K. Macak, G. Mishra, W. Vandervorst IUVSTA-59 Workshop

8:40am **AS1-ThM3 Strategies for Multivariate Analysis of Very Large Spectral Images**, *M.R. Keenan,* Consultant **INVITED**
The sizes of spectral image data sets, always large, are becoming truly huge with modern spectral imaging techniques. Taking ToF-SIMS as one example, image depth profiling can yield data sets comprising several million individual mass spectra arrayed in three spatial dimensions. Spectral complexity is also increasing, particularly in biological applications where more mass channels and higher spectral resolution are required to separate and identify the species of interest. The tools of multivariate statistical analysis (MVA) have proven valuable aids to interpreting complex, high-dimensional data. Given the realities of huge data sets, however, straightforward application of these techniques strains the computing resources available in the typical analytical laboratory. In this paper, we propose a two-stage strategy for multivariate analysis of very large spectral images. In the extraction phase, we seek to efficiently distill the chemical information contained in the data into a minimum number of components that describe the spatial and spectral characteristics the species making up the sample. Principal Component Analysis (PCA) of data suitably preprocessed to account for non-uniform noise is the maximally parsimonious method for extracting information. Techniques for exploiting characteristics of the raw data, such as sparsity, and approaches to estimating the noise covariance on-the-fly can make order-of-magnitude computational improvements in PCA. Owing to the physically irrelevant constraints imposed on the principal components, however, they are notoriously abstract in appearance and difficult to interpret. In the second, or interpretive, stage of MVA, we will perform rotations or transformations of the principal components that are inspired by physically meaningful sample or spectral features such as component non-negativity, sparsity, independence and simplicity. Abstract factor rotations, such as the Varimax method, are time-honored tools in Factor Analysis, but appear to be underutilized in chemometrics. In this talk, we will discuss a general and rapid method for performing factor rotations based on arbitrary optimization criteria. Besides making a connection between factor rotation and seemingly disparate techniques such as Independent Component Analysis (ICA) and Maximum Autocorrelation Factors (MAF), we will present several novel rotations that have potential use in spectral image analysis. An important point, here, is that the rotations entail relatively low computational cost allowing us to examine our results from multiple points of view with an eye toward find representations that best help us solve the chemical problem at hand.

9:20am **AS1-ThM5 Report on the 59th IUVSTA Workshop: Surface Chemical Analysis – Improving Data Interpretation by Multivariate & Informatics Techniques**, *J. Tyler*, University of the West Indies, Trinidad and Tobago

9:40am **AS1-ThM6 Multivariate Analysis of NEXAFS Spectrum Images**, *J.A. Ohlhausen, M.T. Brumbach,* Sandia National Laboratories, *C. Jaye, D.A. Fischer,* NIST, *E. Principe, P. Sobol,* Synchrotron Research, Inc.

Applied Surface Science
Room: Cochiti A - Session AS2-ThM

Forensics, Failure Analysis, and Practical Surface Analysis
Moderator: I.S. Gilmore, National Physical Laboratory, UK

10:40am **AS2-ThM9 Characterization of Composition C4 Explosives using Time-of-Flight Secondary Ion Mass Sepctrometry (ToF-SIMS) and X-Ray Photoelectron Spectroscopy (XPS)**, *C. Mahoney, K.L. Steffens, A.J. Fahey, B.A. Benner,* National Institute of Standards and Technology, *R.T. Lareau,* Transportation Security Laboratory **INVITED**
Over the past decade, we at the National Institute of Standards and Technology have been working closely with the Department of Homeland Security to stop the threat of terrorist-based attacks in the form of explosives or explosive-based devices. Our program encompasses many different aspects of this threat, from development of measurement standards for trace explosives detection at airports, to the development and application of new metrology for the characterization these explosives. Here we present, to our knowledge, the first investigation into the application of surface analytical techniques, such as Secondary Ion Mass Spectrometry (SIMS) and X-Ray Photoelectron Spectroscopy (XPS) for the characterization and differentiation of plastic explosives. This particular work is focused on the characterization of composition C-4 explosives from several different regions.

Unlike traditional analytical techniques such as GCMS and/or LCMS, these powerful surface analytical tools allow for the simultaneous and direct characterization of <u>all</u> the components in C-4 (explosive components, additives, binders, contaminants etc.), as opposed to a partial analysis of extracted portions. Furthermore, the characterization of the explosive samples with ToF-SIMS and XPS will enable rapid identification of both organic and inorganic constituents as well as their characteristic isotopic abundances with excellent sensitivity. Most importantly, these techniques are well-suited for direct analysis of small explosive particulates collected directly in the field, and are already employed for homeland security applications that effect national policy.

11:20am **AS2-ThM11 Chemical Speciation of Engineered Nanoparticle Surface Chemistry with Secondary Ion Mass Spectrometry**, *C. Szakal, R.D. Holbrook,* National Institute of Standards and Technology
As the sizes of nanostructures decrease, the surface-to-volume ratios increase immensely such that the smallest nanoparticles are theoretically seen by their surroundings as only the chemistry exposed on the surface and not the bulk of the nanoparticle interiors. We believe that the ability to track the surface chemistry of nanoparticles vs. size and vs. environmental exposures will show dramatically altered surface chemistry, and thus altered chemical reactivity of the nanoparticles. This concept has widely been suspected and/or believed to be true within the nanoparticle field, but experimentalists have yet to devise a standard approach at measuring what the surface chemistry is and to what extent that surface chemistry can be altered in real-world conditions. Since we are interested *only* in the surfaces of the nanoparticles and not necessarily the bulk, we have worked to develop a new paradigm for monitoring the surface chemistry of engineered nanoparticles with secondary ion mass spectrometry (SIMS). When kept in a static mode analysis, SIMS can be highly surface-sensitive to just a few nm, where other commonly employed techniques for measuring nanoparticle chemistries either cannot separate bulk vs. surface information, or only arrive at surface information indirectly. We will present progress made towards reaching our aims, including nanoparticle preparation considerations, sensitivity of SIMS to monitoring changes in the nanoparticle surfaces, and projections into the future of this methodology for such a purpose.

11:40am AS2-ThM12 Complementary XPS and SEM/EDS Characterization of Gunshot Residue (GSR), *A.J. Schwoeble, B.R. Strohmeier, J.D. Piasecki*, RJ Lee Group, Inc.

Discharged firearm cartridges produce unique microscopic particles referred to as gunshot residue (GSR). GSR is the product of combustion of the primer material. Depending on the type and brand of ammunition, GSR particles typically contain varying amounts of lead, barium, and antimony, along with one or more other elements, such as aluminum, silicon, phosphorus, sulfur (trace), chlorine, potassium, iron (trace), nickel, copper, zinc, zirconium, and tin. If particles containing lead, antimony, and barium are detected on a crime suspect's hands or clothing, it is taken as sufficient evidence that the person has either recently handled a discharged firearm, was present in the general vicinity of a weapon while it was discharged, or came in contact with a surface contaminated with GSR. Scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS) is the most commonly used technique for detecting the presence of GSR particles. GSR samples are collected from a suspect's hands and clothing using adhesives mounted on standard SEM sample stubs. SEM imaging is used to verify the characteristic size, shape, and morphology of GSR particles and EDS can identify the elemental composition of individual particles.

Determining the presence of lead, barium, and antimony fused together in a single particle having the correct morphology is all that is normally required for the positive identification of GSR. However, because of the high temperatures (~1,500-3,600 °C) and pressures (~14,000-65,000 psi) that result within 1 millisecond of discharging a firearm cartridge, highly complicated chemical interactions are likely to occur that will affect the chemical composition of the GSR particles. Because of its nanometer-scale sampling depth and the ability to provide detailed chemical state information, X-ray photoelectron spectroscopy (XPS) can provide important information regarding the surface chemistry of GSR; therefore, XPS offers potential as a complementary technique to SEM/EDS analysis. The aim of this investigation was to use XPS to gain further knowledge regarding the surface chemistry of GSR.

Energy Frontiers Topical Conference
Room: Pecos - Session EN+AS-ThM

Surface and Interface Analysis of Materials for Energy
Moderator: S.M. Han, University of New Mexico

8:00am EN+AS-ThM1 Functionalization of Carbon Materials for the Controlled Deposition of Pt Electrocatalysts for Fuel Cell Applications, *S. Pylypenko*, Colorado School of Mines, National Renewable Energy Lab, *A. Dameron, T. Olson, K.C. Neyerlin, J. Bult, C. Engtrakul*, National Renewable Energy Lab, *A. Queen*, Colorado School of Mines, *K. O'Neill, T. Gennett, H.N. Dinh, B. Pivovar*, National Renewable Energy Lab, *R.P. O'Hayre*, Colorado School of Mines

Catalyst-support interactions are essential in the design of materials for a variety of applications related to renewable energy technologies. In the fuel cell field, improved understanding of these interactions enables controlled improvement in the catalytic activity and durability of carbon-supported fuel cell electrocatalysts. Carbon surface chemistry and structure can be altered to achieve a desired coverage, morphology and composition of the metal nanophase. For example, doping a model HOPG surface with argon or nitrogen results in structural and chemical modification of its surface that leads to improved dispersion, decreased nanoparticle phase and, at certain conditions, enhanced stability. In this work, the role of surface defects, oxygen and nitrogen groups introduced during doping and their effect on electrocatalyst deposition and performance is evaluated through a combination of spectroscopic (XPS, Raman, EELS) and microscopic (SEM, TEM) methods. The same methods are used to evaluate the effect of various surface modifications (via Ar plasma, O_2 plasma and their mixture, HNO_3, TMA functionalization, etc.) on high surface area carbon materials (CNTs, for instance) and their effect on nucleation and growth of Pt in a controlled nanoparticle or continuous coating phase.

8:20am EN+AS-ThM2 Structural and Morphological Properties of Carbon Supports studied by XPS and SEM: Effect on Catalyst Degradation, *A. Patel*, K. Artyushkova, P. Atanassov, University of New Mexico, *A. Young, M. Dutta, Z. Ahmad, V. Colbow, S. Wessel*, Ballard Power Systems, Canada

Understanding the chemical structure and morphology of Pt electrocatalysts and their supports, and linking these parameters to electrocatalytic activity, corrosion stability and overall performance of the fuel cell is essential for elucidation of failure mechanisms and optimization of support properties.

The strategy presented in this work can be viewed as universal methodology that allows correlation between multiple variables relevant to fuel cell technology.

In this work we have investigated the performance and corrosion stability of Pt electrocatalysts supported on different carbon supports in order to understand the effect of the carbon support on catalyst degradation. Low surface area (LSA), mid-range surface area (MSA), high surface area (HSA) and heat treated (to induce graphitization) high surface area carbons were extensively studied and characterized.

X-ray Photoelectron Spectroscopy (XPS) has been chosen to obtain information on graphiticity and amount of surface oxides on carbon supports. The ability to discriminate between different carbon chemical environments, not just elemental compositions, is one of the primary advantages of XPS in the characterization of carbon corrosion.

Morphological properties such as size of particles, size of particles agglomerates, surface area, roughness and porosity are equally contributive to corrosion process. Digital Image Processing (DIP) can be applied to SEM and TEM images to extract statistical parameters, such as roughness, particle size distributions, shape parameters, texture parameters, which all are related to morphology of carbon blacks.

Performance and durability of Pt electrocatalysts supported on various carbon blacks were evaluated extensively electrochemically to provide activity from rotating disk electrode measurements, capacitance and photon resistance from Electrode Impedance Spectroscopy, voltage degradation rates, effective platinum surface area and kinetic losses.

This multi-analytical approach provides a large set of variables (structural, physical and microscopic properties) which must be related to corrosion and performance behaviour of carbon blacks. Multivariate statistical methods of data analysis (MVA) become, thus, of critical importance in structure-to-property relationship modeling. Principal Component Analysis (PCA) is used as a visualization tool to find samples which are globally correlated or anti-correlated, and to facilitate visualization of the variables responsible for the correlations. Through this methodology, we have determined which set of structural and morphological parameters are responsible for durable and active electrocatalyst.

8:40am EN+AS-ThM3 Anchoring of N3, N719 and Z907 Dye Molecules on TiO$_2$(110) Surface, *P. Nachimuthu*, A. Pandey, Z.Q. Yu, Z.H. Zhu, K.M. Beck, S. Thevuthasan, M.A. Henderson, D.R. Baer, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the alignment of the energy levels for the dye and TiO$_2$ resulting from the electronic coupling between these states determines the photoinduced electron transfer across the dye-TiO$_2$ interface. The electronic coupling which in turn is strongly modified by the mode of binding of the dye molecules onto TiO$_2$ surface, its relative orientations and geometrical structures. In order to understand the mode of binding of the dye molecules on TiO$_2$(110) surface, the N3, N719 and Z907 dye molecules in the powder form and adsorbed on TiO$_2$(110) surface using 0.25-1.0 mg/ml in ethanol were investigated using high-resolution x-ray photoelectron spectroscopy. The S 2p XPS data from N3 dye molecules adsorbed onto TiO$_2$ surface show two S components in addition to SO$_x$ suggesting that the S atoms in the –NCS functional groups exist in two different chemical environments with a binding energy difference of ~1 eV and the intensity ratio of ~1 indicating that in each intact N3 molecule on TiO$_2$, one –NCS group is bound to TiO$_2$(110) surface and the other is projected away from TiO$_2$ surface. The O 1s XPS data show components at 531.2 eV and 533.1 eV which are arising from C=O / COO$^-$ and C-OH bonds from carboxylic acid groups in N3 molecule, respectively, in addition to a peak at 529.7eV from TiO$_2$. The relative intensity ratio of the O 1s XPS components at 533.1 eV to 531.2 eV signifies the presence of protonated carboxylic acid groups in N3 molecule and is found to be 0.388 suggesting that only one carboxylic acid group in each N3 molecule is deprotonated and it is most likely bound to TiO$_2$ surface. In contrast, both the -NCS groups in the N719 and Z907 dye molecules were projected away from the TiO$_2$ surface and are not involved in binding with TiO$_2$ surface. One of the carboxylic acid groups in Z907 is deprotonated and it is most likely bound to TiO$_2$ surface. Furthermore, with decreasing the dye concentration in ethanol results in a gradual dissociation of –NCS groups from Ru in these dye molecules.

9:00am EN+AS-ThM4 Characterization of Minority Carrier Lifetime in Ge Films Epitaxially Grown on Si by Nanoscale Interfacial Engineering, *J.J. Sheng*, D. Leonhardt, University of New Mexico, *J.G. Cederberg, M.S. Carroll*, Sandia National Laboratories, *M.J. Romero, S. Johnston*, National Renewable Energy Laboratory, *S.M. Han*, University of New Mexico

High-quality Ge-on-Si (GoS) heterostructures are pursued for many applications, including near infrared (NIR) photodetectors and integration with III-V films for multijunction photovoltaics. However, such integration

poses many engineering challenges, ranging from lattice mismatch, to thermal expansion coefficient mismatch, to non-planar morphological evolution. We have previously demonstrated a scale-up of growing low-dislocation-density Ge on Si by manipulating the Ge-Si interface at the nanoscale, using a thin chemical SiO_2 layer and a surface reaction involving Ge and SiO_2. We have also developed a slurry-free, chemical-mechanical polish step to planarize the GoS surface resulting in a Ge surface with a root mean square (RMS) roughness of less than 1 nm. Herein, we focus on the characterization of carrier lifetime in the Ge epilayers grown on Si by the said nanoscale Ge-Si interfacial engineering. Using photoconductivity decay techniques, minority carrier lifetime is measured in the GoS substrates to extract surface recombination velocity as well as carrier lifetime in bulk Ge. The effective surface recombination velocity, representing both Ge-Si interface decorated with chemical SiO_2 and Ge surface, is approximately $1.26x10^4$ cm/sec, largely dominated by recombinations at the oxide. We observe that the extracted lifetimes, which vary with the Ge film thickness, correlate well with the dislocation density that varies as a function of distance from the Ge-Si interface. In this presentation, we will further discuss capacitance-voltage characterization of metal-oxide-semiconductor structures fabricated on our GoS substrates.

9:40am EN+AS-ThM6 A Multi-technique Approach to the Characterization of New Materials for Energy Production, *T. Nunney, R.G. White, N. Bulloss, P. Camus, J. Konopka,* ThermoFisher Scientific, UK, *H.M. Meyer III*, Oak Ridge National Laboratory

In order to meet the challenges of more economical and environmentally benign energy production, a new generation of complex materials and devices is being developed, these include thin film solar cells, fuel cells, and batteries. In all stages of development there is a requirement for materials characterization and analysis; from the initial development stages, through to testing of the finished article. Most materials need to be analyzed for compositional homogeneity across the sample surface and also for layer chemistry, interface chemistry and thickness through the sample. It is rare that a single technique can achieve all of these testing requirements, and therefore a complementary approach involving several techniques is demanded.

In this presentation we will discuss how a multi-technique approach can address a variety of technical problems, illustrated by examples from real applications case studies. We will mainly concentrate on the information supplied from two techniques, XPS and EDS, but we will also consider the additional data that can be obtained from other sources such as Raman spectroscopy.

X-ray photoelectron spectroscopy (XPS) is ideally suited to the quantitative determination of the surface chemistry and the way in which that chemistry changes in the surface, near-surface and interface region of the materials.

Energy Dispersive Spectroscopy (EDS) collects characteristic X-rays generated by rastering an electron beam over a solid sample to generate a full elemental X-ray spectrum at each pixel of the electron image. The latest generation silicon drift detectors for EDS are capable of collecting and storing hundreds of thousands of X-ray counts per second. This large volume of X-ray data, collected across the sample, allows for rapid identification and characterization of surface defects and lateral compositional variations. Software advances now allow rapid, multivariate statistical analysis processing of very limited amounts of X-ray data to determine not only the elemental distribution across the sample but also the chemical phase distribution.

10:40am EN+AS-ThM9 Novel Visible-Light Photo-Sensitive Zirconium Oxynitride (ZrO_xN_y) Thin Films, *C.V. Ramana, N.E. Esparza, I. Fernandez,* University of Texas at el Paso, *A.L. Campbell,* Wright Patterson Air Force Base

Zirconium oxide (ZrO_2) exhibits excellent optical properties such as high refractive index, large band gap, low optical loss, high transparency in the visible and near-infrared regions, and high dielectric constant. However, ZrO_2 is UV-light sensitive. In addition, interfacial reactions during thin-film growth suppress the effective dielectric constant and degrade the optical performances. The present work was performed on ZrO_xN_y thin films to effectively alter the electronic structure by the method of nitridation, which well-known to suppress the interfacial reactions. ZrO_xN_y thin films were produced by magnetron-sputter deposition under the reactive pressure of nitrogen and oxygen. The effect of nitrogen/oxygen flow rate on the structure and optical properties of ZrO_xN_y thin films was investigated and compared with that of ZrO_2. The optical measurements of ZrO_2 films show a very high optical transmission with a band gap of 5 eV. The optical absorption measurements on ZrO_xN_y thin films grown at various reactive nitrogen pressures indicate a progressive shift from insulating to semiconductor behavior. The corresponding changes in the profiles of index of refraction were also remarkably distinct. The results indicate that tailoring the electronic structure and optical constants of ZrO_xN_y thin films

to meet the requirements of visible-light functionality can be achieved by carefully controlling the reactive pressure. The results will be presented and discussed in detail.

11:00am EN+AS-ThM10 Quantification of Hydrogen and Deuterium in Niobium and Niobium Oxide, *P. Maheshwari,* **F.A. Stevie**, North Carolina State University, *G.R. Myneni, G. Ciovati,* Jefferson Lab, *M. Rigsbee, D.P. Griffis*, North Carolina State University

Superconducting Radio Frequency (SRF) cavities provide enhanced efficiency and reduced energy utilization in present day particle accelerators. Niobium (Nb) is the material of choice for these cavities due to its high critical temperature and critical magnetic field**.** In order to understand why certain treatments, especially a low temperature bake, improve performance, it is important to study Nb surface characteristics and identify elemental contamination that can affect the performance of the cavity. H, C, O, and N are of interest because they are interstitial impurities in Nb. In earlier work,[1] SIMS analysis using a CAMECA IMS-6F with Cs+ primary beam showed that C and N were probably not significant factors impacting performance and that there was a very high level of H in the Nb. TEM analysis also showed that the surface niobium oxide was a uniform layer with typical thickness about 6nm. Ion implants of C, N, O, and D into Nb provided quantification of C, N, O and indicated that D is very mobile in the Nb.[2]

Analysis of samples before and after heat treatment showed that the H level could be dramatically reduced after certain heat treatments. Removal of the oxide with HF caused the H to return to its former level and the native oxide was again established. SIMS measurement of H in the niobium oxide showed a low H level and, as noted above, the oxide appears to be a very effective H barrier. One possible cause for the removal of H by low temperature heat treatment is the possible formation of openings in the oxide barrier which allows the hydrogen to exit the Nb surface, followed by the renewal of the oxide after heat treatment which does not allow H to re-enter. Another theory is that the heat treatments drive the H deeply into the Nb.

In order to better understand the role of the niobium oxide, implants have now been made into a specially prepared 120nm thick niobium oxide layer on Nb substrate. H is shown to have an implant shape in the oxide and verify that H is not mobile in the oxide. An implant of D with peak at the oxide/Nb interface showed an implant shape up to the interface and a sharp drop once the Nb was reached. If the H relative sensitivity factor from the oxide is used to quantify the H in a Nb sample without heat treatment, the H concentration is measured as 2E22atoms/cm3.

[1] A. D. Batchelor, D. N. Leonard, P. E. Russell, F. A. Stevie, D. P. Griffis, G. R. Myneni, Proceedings of Single Crystal Niobium Technology Workshop, Brazil, AIP Conference Proceedings, Melville, NY (2007) 72-83.

[2] P. Maheshwari, H. Tian, C. Reece, G. Myneni, F. Stevie. M. Rigsbee, A. Batchelor, D. Griffis, Surf. Int. Anal. (in press 2010)

11:20am EN+AS-ThM11 Study of Thin Film Solar Cell Materials using Variable-Wavelength Electric Force Microscopy, *J. Luria, J.J. Choi, T. Hanrath, J.A. Marohn*, Cornell University

Organic electronics offer a clear path to large scale, low cost photovoltaics. But efficiency issues such as charge transport, extraction, and device degradation keep these materials from being market-viable. Electric Force Microscopy (EFM) allows us to probe electronic properties of various materials and meso-scale morphologies. By observing the photo-induced response and degradation, we are able to inform synthetic and fabrication processes.

We have developed a general approach to illuminate samples in our custom-built vacuum electric force microscope. We will describe experiments using variable-wavelength light to characterize lead sulfide, PFB/F8BT polymer blend, and other thin film photovoltaic devices.

Graphene Focus Topic
Room: Brazos - Session GR+AS+TF-ThM

Graphene Synthesis on Metals
Moderator: A.W. Ghosh, University of Virginia

8:00am GR+AS+TF-ThM1 Contrast Behavior of Carbon Adatom Diffusion and Nucleation in the Initial Stage of Graphene Epitaxial Growth on Stepped Metal Surfaces, *H. Chen*, *W. Zhu*, University of Tennessee at Knoxville; Oak Ridge National Laboratory, *Z. Zhang*, Oak Ridge National Laboratory; University of Tennessee at Knoxville
Using first-principles calculations within density functional theory, we study the energetics and kinetics of carbon adatom diffusion and nucleation on three stepped metal surfaces: Ir(111), Ru(0001) and Cu(111). We find that on the flat surfaces, two carbon atoms repel each other on Ir(111) and Ru(0001), while they prefer to form a dimer on Cu(111). Moreover, the step edges on Ir and Ru surfaces cannot effectively trap single carbon adatoms either, whereas it is strongly favorable to form carbon dimers at the step edges. The different behaviors are attributed to the competition between C-C bonding and different types of C-metal bonding, and the picture is generalized to other C-on-metal systems with predicted results. These findings provide an insight into the understanding of experimentally observed carbon nucleation in the initial stage of graphene epitaxial growth on metal surfaces.

8:20am GR+AS+TF-ThM2 Density and Height Distribution of Ru and Bimetallic Pt/Ru Nanoclusters Self-Assembled on Ru(0001) Supported Monolayer Graphene, *A.K. Engstfeld*, *S. Beckord*, *H.E. Hoster*, *R.J. Behm*, Ulm University, Germany
The Moiré-type nm-scale patterns of graphene monolayers on metal single crystals were recently shown to allow facile fabrication of ordered arrays of virtually monodisperse metal nanoclusters by simple metal vapour deposition in UHV [1-3]. In view of a potential utilization as model systems in electrocatalysis, we have tested the possibility of preparing Ru and bimetallic PtRu clusters by an analogous procedure. This included an extended study on the growth behaviour of the pure Ru clusters. Statistically evaluated STM images indicate that density and height distribution of Ru clusters are largely independent from the evaporation rate at room temperature. Lower/higher cluster densities along with larger/smaller cluster sizes were only achieved by higher/lower substrate temperatures during evaporation. For a given temperature, the lateral density of Ru clusters his higher than that of Pt clusters. Hence, the fabrication of bimetallic clusters can be performed more reliably when Ru is deposited first. We discuss in how far the found growth behaviour can be understood using classic nucleation theory.

8:40am GR+AS+TF-ThM3 From Perfect Graphene to Cluster Superlattices, *T. Michely*, University of Cologne, Germany **INVITED**
Through pyrolysis of hydrocarbons on noble metal surfaces monolayer graphite – graphene – is readily formed. Using scanning tunneling microscopy (STM) and low energy electron microscopy (LEEM) we investigate the temperature dependent growth and the nature of point and line defects in the graphene layer on Ir(111). We identify heptagon-pentagon pairs of carbon atom rings to accommodate for slight misalignments of graphene domains, and wrinkles in the graphene layer for the mismatch in thermal expansion of graphene and Ir. After a systematic optimization of the growth procedure we obtain a single sheet of well oriented graphene on Ir(111) with a minimum of point and line defects.

Angle resolved photo emission finds graphene on Ir(111) to be only marginally doped and to display the characteristic Dirac cone at the K-point of the graphene Brillouin zone. The absence of hybridization of Ir and graphene states is consistent with the weak graphene - Ir interaction, as inferred from the large graphene - substrate separation as measured by the X-ray standing wave method and calculated by density functional theory including van der Waals interactions. The moiré resulting from the incommensurate epitaxy of graphene on Ir(111) gives rise to a large graphene supercell. In the graphene electronic structure it is reflected by the opening of minigaps at the boundaries of the induced mini-Brillouin zone.

The graphene moiré with Ir(111) is an active template allowing one to grow superlattices of metal clusters (Ir, Pt, Au, W, Fe, Re, Co, etc), spatially and thermally stable below 450 K. The graphene moiré enables also patterned adsorption of molecules and the template effect is not limited to the Ir(111) substrate. Based on STM and XPS measurements as well as density functional theory calculations it is proposed that at geometrically defined locations within the supercell and if sandwiched between substrate and cluster metal the graphene rehybridizes from sp^2 graphitelike to sp^3 diamondlike bonding, resulting in strong covalent bonds between metal and graphene. The relevance of the graphene template effect for nanocatalysis, nanomagnetism and electrochemistry will be outlined.

9:20am GR+AS+TF-ThM5 Graphene on Pd(111): *In situ* **Low-Energy Electron Microscopy Studies of Growth Kinetics and Structure – Work Function Relationship**, *S. Kodambaka*, *Y. Murata*, University of California Los Angeles, *E. Starodub*, *N.C. Bartelt*, *K.F. McCarty*, Sandia National Laboratories
Using *in situ* low-energy electron microscopy, we investigate the dynamics of graphene layer formation and the relationship between domain structure and its work function on Pd(111). We observe, in real time, the nucleation and growth of graphene islands during cooling via surface segregation of C atoms from the Pd bulk. Interestingly, we observe rapid motion of Pd substrate surface steps during graphene growth. Using low-energy electron diffraction, we identify at least five different orientations (domains) of monolayer graphene islands on the surface. We determine their relative orientations with respect to the substrate as approximately 2°, 6°, 11°, 19°, and 26°. We measured electron reflectivity (image intensity) values for each of the domains as a function of incident electron energy. From this data, we extracted the work functions of graphene domains which are found to vary with the domain orientation. Our results suggest that the substrate-graphene interactions influence the growth kinetics as well as the electronic structure of graphene.

9:40am GR+AS+TF-ThM6 Second-Layer Graphene on Ir(111) – Relating Growth Mechanism to Physical and Electronic Structure, *S. Nie*, Sandia National Labs, *A.L. Walter*, Lawrence Berkeley National Lab and Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *E. Starodub*, **K.F. McCarty**, *K. Thürmer*, Sandia National Labs, *K. Horn*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *A. Bostwick*, Lawrence Berkeley National Lab, *N.C. Bartelt*, Sandia National Labs, *E. Rotenberg*, Lawrence Berkeley National Lab
An interesting question is how the second layer of graphene grows on transition-metal substrates. First-layer graphene on Ir(111) [1] exists with four discrete in-plane orientations relative to substrate directions [2]. Thus, this system offers potential to better understand the relationship between second-layer growth and first-layer structure. We use low-energy electron microscope (LEEM) to characterize where the second-layer graphene forms on Ir(111) covered by domains of differently oriented first-layer graphene. We find that the second layer does not grow easily where the lattice of the first-layer graphene is aligned with the lattice of the substrate. Instead the second-layer graphene forms most easily where the first-layer graphene is rotated, by 30°, for example. Angle-resolved photoemission spectroscopy (ARPES) confirms this strong preference. So how does the orientation of the first layer control the growth of the second layer? ARPES and Raman spectroscopy provide insight, revealing that the rotated variants of first-layer graphene are even less strongly bound to the substrate than the more abundant, non-rotated variant [3]. This information suggests the following growth mechanism. Carbon atoms segregating from the substrate build up in concentration under the first layer. The second layer nucleates and grows where it is easier to debond the first layer from the substrate, that is, under the rotated first-layer domains. Electron diffraction also reveals that the second graphene layers are usually but not always aligned with the first-formed layer. Finally, we will discuss the doping of the different types of second-layer graphene, as revealed by ARPES.

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10:40am GR+AS+TF-ThM9 Graphene on Transition Metals – Growth and Interfacial Processing, *P. Sutter*, *E. Sutter*, Brookhaven National Laboratory **INVITED**
Graphene has been used to explore the fascinating properties of two-dimensional sp^2 bonded carbon, and shows great promise for applications. A key bottleneck lies in synthesizing the required starting material: structurally perfect, macroscopically large graphene sheets with uniform thickness, into which active device structures can be patterned.

Epitaxial growth on transition metals has recently become one of the most promising methods for large-scale graphene synthesis. Here we discuss the fundamental mechanisms of graphene growth on ruthenium [1] and platinum [2], both single crystals and polycrystalline thin films, studied by a combination of *in-situ* surface microscopy methods. Real-time observations

by low-energy electron microscopy (LEEM) show that epitaxy on Ru(0001) produces arrays of macroscopic monolayer graphene domains, whose coalescence is followed by the formation of large bilayer areas in a controlled layer-by-layer fashion. LEEM imaging together with diffraction, selected-area angle resolved photoemission spectroscopy (micro-ARPES), and scanning tunneling microscopy provide unique insight into the interaction between graphene and transition metal substrates, key to the synthesis of high-quality graphene [2, 3].

Beyond large-scale synthesis, potential applications of graphene will require novel approaches to processing and functionalization. We will highlight experiments by real-time surface microscopy to understand chemical reactions at graphene-metal interfaces, which may become part of novel processing strategies for graphene devices.

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[3] P. Sutter, M.S. Hybertsen, J.T. Sadowski, and E. Sutter, Nano Lett. **9**, 2654 (2009).

11:20am GR+AS+TF-ThM11 Real-time Analysis of Graphene Growth on Polycrystalline Copper Foils, *J.M. Wofford,* University of California at Berkeley and Lawrence Berkeley National Lab, *S. Nie, N.C. Bartelt, K.F. McCarty,* Sandia National Laboratories, *O. Dubon,* University of California at Berkeley and Lawrence Berkeley National Lab

Despite the potentially significant technological impact of graphene synthesis on Cu, little is understood about both the growth kinetics of this system and the morphology of the resulting heterostructure. We use low-energy electron microscopy (LEEM) to observe directly the UHV growth of graphene on polycrystalline Cu foils by the electron-beam evaporation of carbon. The temperatures required to synthesize highly ordered graphene simultaneously induce significant Cu sublimation and step flow, leading to a dynamic growth surface. As a result a complex interdependence develops between the graphene growth behavior and Cu surface morphology, with the graphene islands limiting Cu step mobility, and Cu step bunching distorting the propagation of the graphene growth front. This interplay becomes increasingly dramatic over time as the inhomogeneous sublimation of Cu leads to considerable surface roughening. In addition, the graphene islands are not compact in shape. Instead, the islands are ramified, consisting of several distinct lobes extending from a common nucleation site. Diffraction analysis reveals that each constituent lobe has a different in-plane orientation relative to the copper grain below and that the growth velocity of a given lobe depends strongly on its orientation relative to the underlying Cu at the growth front. We will describe the relationship between the orientation-dependent growth velocity and the local atomic geometry at the edge of the graphene sheet. Finally, the implications of this unexpected nucleation and growth mechanism on the formation of high-quality graphene films on Cu foils are evaluated.

11:40am GR+AS+TF-ThM12 Moiré Superstructures of Graphene on Facetted Nickel Islands, *Y. Murata,* University of California Los Angeles, *V. Petrova,* University of Illinois at Urbana-Champaign, *B.B. Kappes, A. Ebnonnasir,* Colorado School of Mines, *I. Petrov,* University of Illinois at Urbana-Champaign, *Y.-H. Xie,* University of California Los Angeles, *C.V. Ciobanu,* Colorado School of Mines, *S. Kodambaka,* University of California Los Angeles

Using scanning tunneling microscopy and spectroscopy, in combination with density functional theory (DFT), we investigated the morphology and electronic structure of monolayer graphene grown on the (111) and (110) facets of three-dimensional nickel islands on highly oriented pyrolytic graphite substrate. We observed hexagonal and stripe moiré patterns with periodicities of 22 Å and 12 Å, respectively, on (111) and (110) facets of the Ni islands. Graphene domains are also observed to grow, as single crystals, across adjacent facets and over facet boundaries. We suggest that the unexpected observation of moiré patterns of graphene on lattice-matched Ni(111) and the formation of single-crystalline domains across different surface orientations are a consequence of the kinetic limitations of growth, rather than of the strength of the C-Ni interactions. Scanning tunneling spectroscopy data indicate that the graphene layers are metallic on both Ni(111) and Ni(110), in agreement with the DFT calculations. We attribute this behavior to strong hybridization between the d-bands on Ni

and the p bands of carbon. Our findings point to the possibility of preparing large-area epitaxial graphene layers even on polycrystalline Ni substrates.

Thursday Afternoon, October 21, 2010

Spectroscopic Ellipsometry Focus Topic
Room: Cochiti - Session EL+AS+EM+MS+TF-ThA

Spectroscopic Ellipsometry
Moderator: A.M. Creatore, Eindhoven University of Technology, the Netherlands

2:00pm **EL+AS+EM+MS+TF-ThA1 Developments in Spectroscopic Ellipsometry for Characterization of Organic and Inorganic Surfaces, Interfaces and Complex Layered Materials**, *M. Schubert*, University of Nebraska - Lincoln **INVITED**
In this paper we will review new developments in Spectroscopic Ellipsometry for characterization of organic and inorganic surfaces, interfaces and complex layered materials. Ellipsometry has matured over the past two decades with instrumentation and methodology capable of addressing today's and tomorrow's challenges in materials characterization and metrology. Ellipsometry measures the general state of polarization of light reflected or transmitted from samples. Owing to its nondestructive and generally applicable concept of investigating light emerging from specimens under investigations, and owing to its extreme accuracy and precision, ellipsometry has paved the way for almost all our modern technologies, continues to enable next-generation devices in electronics and optoelectronics, and emerges into fields of chemical, biochemical and biological platform technologies. Originating from the identification that the information carried upon the polarization within a light beam emerging from surfaces is extremely sensitive to mono and submonolayer characteristics, ellipsometry started decades ago pioneering development of microprocessors and electronic devices, which still today are based on planar thin film technology. Without ellipsometry, today's computation and information technology would be still in its infancy. In this paper, emerging developments and applications for metrology of optical and electrical properties of semiconductors and nanostructures by Terahertz Magnetooptic generalized ellipsometry, also referred to as the Optical Hall effect, will be highlighted. Examples will include state-of-the-art nitride semiconductor device structures and epitaxial graphene, candidates for tomorrow's next-generation devices. Likewise, new approaches for characterizing precise structural, magnetic and optical properties of three-dimensional nanostructure hybrid materials will be discussed. Examples will describe how ellipsometry characterization enables understanding and tailoring of electromagnetic properties of materials created by human intelligence, rather than by nature. New horizons are being explored currently by combining ellipsometry with independent surface sensitive techniques, such as acoustic Quartz-Crystal microbalance techniques. Combinations allow for identification of new information not accessible otherwise. Examples include observation of in-situ formation of self-assembled monolayers, protein adsorption onto sensitized surfaces, and formation of micelle-assisted bilayer configurations. Prospects, challenges and future developments will be reviewed from today's perspective.

2:40pm **EL+AS+EM+MS+TF-ThA3 Characterizing the Adsorption – Desorption Behavior of Organic Molecules Within Thin Mesoporous Carbon Composite Films using Spectroscopic Ellipsometry**, *B.D. Vogt*, *L.Y. Song, M.Z. Dai*, Arizona State University
Porous carbon materials are commonly utilized as adsorbants (i.e. activated carbon) and as catalyst supports. Direct templated synthetic routes to form ordered mesoporous carbons have recently been developed. By utilizing these concepts, mesoporous carbon composite films containing metal oxides can be synthesized. As a wide range of metal oxides can be utilized, these materials could be utilized in chemical sensing applications or as catalysts in fuel cell membranes. For both of these applications, the porous material will be exposed to organic vapors (such as ethanol in fuel cells). The condensation and evaporation of organic vapors from these materials is therefore an important consideration for their ultimate utilization in these applications. In-situ spectroscopic ellipsometry measurements of the mesoporous films exposed to controlled vapor pressures of organic vapors such as toluene, hexane and ethanol are utilized to understand the adsorption-desorption behavior of these films. Activated desorption of all three compounds is observed for pure carbon films, but addition of a small fraction of metal oxide enables the organics to be desorbed for the porous framework. These adsorption-desorption isotherms can also be utilized to estimate the pore size distribution and porosity of these films.

3:00pm **EL+AS+EM+MS+TF-ThA4 Mueller-Matrix Ellipsometry Studies of Chirality in Chitin-Based Structures and Thin Films of Al$_{1-x}$In$_x$N**, *K. Järrendahl*, *H. Arwin, R. Magnusson, P. Sandström, C.-L. Hsiao, J. Landin, S. Valyukh, J. Birch*, Linköping University, Sweden
A limited number of natural structures are known to reflect light that has circular or near circular polarization. This is for instance, the case for some scarab beetles were it is suggested that the polarization is caused by chiral structures in the form of helicoids in the cuticles . In this study, Mueller-matrix spectroscopic ellipsometry is applied in the spectral range of 250 to 1000 nm to investigate optical response and structures of the cuticle of various scarab beetles of the Cetoniinae subfamily. We will present our measurements showing how the polarization changes with wavelength as well as incidence angle and specify the conditions for when the reflected light is circularly left- or right-polarized. In most cases the reflected light is left-polarized as described by negative values of the M41 Mueller matrix element. For *Cetonia aurata*, a green beetle with metallic appearance, this is clearly seen in a rather narrow spectral range (470-550 nm). For other beetles (*Potosia cuprea* and *Licola lugubris*) similar polarization behavior is observed but the polarization features occur in a broader spectral region. We will show that there are even beetles (e.g. *Plusiotis argentiola*) reflecting both left- (M41 < 0) and right-polarized light (M41 > 0) in different parts of the spectral region. The Mueller data, including observations of the degree of polarization, are used to obtain structural and optical parameters from model calculations.

Our attempts to fabricate artificial structures with similar polarization properties will also be presented. Al$_{1-x}$In$_x$N thin films were grown on sapphire substrates by magnetron sputtering of indium and aluminum in a nitride atmosphere. Utilization of different seed layers and a substrate rotation gave chiral structures constituted by layers with a compositional gradient. Mueller-matrix results from these structures will be compared with the results from the natural structures. The Mueller data is also in this case very rich on information. In the initial steps to model these samples a similar approach as for the natural structures has been employed. Similarities and differences of the natural and artificial polarization response will be discussed in detail.

3:40pm **EL+AS+EM+MS+TF-ThA6 Mueller Polarimetry as a Tool for the Evaluation of the Diffraction Grating Profile Asymmetry**, *T. Novikova*, *P. Bulkin*, LPICM, CNRS, Ecole Polytechnique, France, *V. Popov*, Moscow State University, Russia, *A. De Martino*, LPICM, CNRS, Ecole Polytechnique, France
Mueller polarimetry in conical diffraction has proved to be a powerful optical technique for the metrological characterization of diffraction gratings. It was already shown that the shape of grating profile can be successfully reconstructed via appropriate optical modeling using full Mueller matrix measurements [1]. We also demonstrated that this approach can be of particular interest in microelectronics technology for the detection of overlay errors, which frequently result from the alignment deficiencies in lithography [2]. In some cases the asymmetrical distortion of grating profile can be induced by the etch process, or even be intentional, like in blazed gratings fabrication. For these applications a technique that allows for fast non-contact evaluation of the profile asymmetry may be of great value.

We studied the Mueller matrix spectra of symmetrical [3] and asymmetrical photoresist diffraction gratings on chromium using MM16 spectroscopic polarimeter, commercially produced by Horiba Jobin-Yvon, in the most general geometry of conical diffraction. At this configuration the 0th order cross-polarization complex reflection coefficients are antisymmetrical ($r^0_{sp} = -r^0_{ps}$) , provided that the grating is composed of only reciprocal materials and is invariant under the rotation by 180° about the normal incidence [4]. It leads to the following relations between the elements of 2x2 off-diagonal blocks of Mueller matrix: $M_{ij} = \pm M_{ji}$.

The lack of rotational symmetry violates the electromagnetic reciprocity theorem for the 0th-order diffraction on the asymmetrical gratings and, consequently, breaks the symmetry of the off-diagonal blocks of Mueller matrix ($|M_{ij}|$ is not equal to $|M_{ji}|$). This property of Mueller matrix of asymmetrical gratings was experimentally observed and numerically modeled at any illumination condition with exception of planar and pure conical mounting. We showed that the non-reciprocity in diffraction gratings can be used for the unambiguous detection of the grating profile asymmetry. The optimal choice of measurement configuration, i.e. azimuthal and polar angles considerably increases the sensitivity of the above mentioned technique.

References:

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4:00pm EL+AS+EM+MS+TF-ThA7 Monitoring Ultra-Thin Organic Film Growth, *In-Situ*, with Combined Quartz Crystal Microbalance and Spectroscopic Ellipsometry, *K.B. Rodenhausen, B.A. Duensing, A.K. Pannier, M. Schubert,* University of Nebraska-Lincoln*, M. Solinsky,* The Procter & Gamble Company*, T.E. Tiwald*, J. A. Woollam Co., Inc.

We report a combinatorial approach to study ultra-thin organic films. This novel technique consists of *in-situ* spectroscopic ellipsometry and quartz crystal microbalance methods. In contrast to the quartz crystal microbalance, which is sensitive to the total mass attached to the surface, including the trapped solvent, spectroscopic ellipsometry only measures the amount of adsorbent on the surface. We also introduce a new "virtual separation approach" ($2\pi nd/\lambda \ll 1$) of analysis for the ellipsometry measurements. By using these two techniques in tandem, we are able to determine the thickness and solvent fraction of viscoelastic thin films.

We investigate cetyltrimethylammonium bromide (CTAB) thin films deposited onto a gold-coated quartz crystal as a model system. CTAB grown from a 2.5 mM solution demonstrates several phases in porosity evolution, including a temporary hold in water fraction as the film is rinsed off the substrate with water; these effects may be related to the structure of a CTAB bilayer.

In addition, a variety of self-assembled monolayers (SAMs) of alkanethiols on gold-coated quartz crystals are used as model biomaterials to determine the water fraction of an adsorbed prion layer. The porosity information distinguishes the proteins' conformation, dictated by the defined surface chemistries of the SAMs.

4:20pm EL+AS+EM+MS+TF-ThA8 Ellipsometric Studies of Electronically Coupled PbSe and PbS Quantum Dot Thin Films, *S.G. Choi,* National Renewable Energy Laboratory*, O.E. Semonin,* University of Colorado*, J.M. Luther, M.C. Beard, A.G. Norman,* National Renewable Energy Laboratory*, Z. Lin,* Colorado School of Mines*, A. Franceschetti,* National Renewable Energy Laboratory*, M.T. Lusk,* Colorado School of Mines*, A.J. Nozik*, National Renewable Energy Laboratory

Discovery of multiple exciton generation from colloidal suspensions of semiconductor quantum dots (QDs) has generated growing interests in realization of high-efficiency QD-based solar cells. Among a number of semiconductor QDs explored up to date, lead chalcogenides such as PbSe and PbS have been of great interest as a result of their wide tuning range of bandgap energy, abundance of materials, and large exciton Bohr radius.

In this presentation, I discuss optical properties of electronically coupled PbSe and PbS QD thin films. A series of QD multilayer thin films were prepared by a layer-by-layer dip-coating method onto glass substrates. Diameter of the QDs varies from 3.2 to 7.2 nm and from 3.5 to 8.3 nm for PbSe and PbS, respectively. Room-temperature pseudo-optical functions of the samples were measured by a rotating compensator-type, variable-angle spectroscopic ellipsometer. Transmittance data were also acquired in a normal-incidence configuration.

First, I determined refractive index $N = n + ik$ of the QD films using the B-spline basis functions within the multilayer model (ambient/surface roughness/QD film/substrate). We use the N obtained as the input parameters for modeling the internal quantum efficiency of the QD-based solar cell devices. Then, I extracted dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ for the ensemble of electronically coupled QDs using the Maxwell-Garnett effective medium approximations. The ε spectra show the first exciton peaks, and the E_1 and E_2 critical-point (CP) structures whose energies are higher than the corresponding bulk values probably due to the quantum confinement effects. This abstract is subject to government rights.

4:40pm EL+AS+EM+MS+TF-ThA9 In-situ Temperature Measurements by Spectroscopic Ellipsometry: Application to a-Si based Thin Films, *D. Daineka,* LPICM, CNRS, Ecole Polytechnique, France*, V. Suendo,* Institut Teknologi Bandung, Indonesia*, P. Roca i Cabarrocas*, LPICM, CNRS, Ecole Polytechnique, France

Accurate measurement of the substrate temperature is of crucial importance in many semiconductor technologies such as plasma enhanced chemical vapor deposition (PECVD). Traditional tools, both thermocouples and pyrometers, are not always reliable for in situ measurements in vacuum when the substrate can be out of thermal equilibrium. On the other hand, non-contacting optical methods allow to determine the surface temperature with great accuracy, provided the temperature dependence of optical constants for the studied material is known. Since recently, spectroscopic ellipsometers are widely available and often installed on the research deposition systems, which provides an opportunity to use them for temperature monitoring. We have studied the optical functions of amorphous silicon based thin films with spectroscopic ellipsometry in the temperature range from 290 to 520 K. The experimental data were modeled using Tauc-Lorentz dispersion law for amorphous materials. We have found that the temperature coefficients of Tauc-Lorentz parameters, such as the optical gap, are rather close for a few different materials. That similarity suggests that these values can be used to determine the surface temperature for a broad range of amorphous silicon based materials with a good accuracy. Practical examples of using spectroscopic ellipsometry for temperature measurements in the low pressure PECVD environment are given.

5:00pm EL+AS+EM+MS+TF-ThA10 Real Time Spectroscopic Ellipsometry Studies of Amorphous and Nanocrystalline Si₁₋ₓGeₓ:H Thin Films for Microbolometer Applications, *D.B. Saint John, H.-B. Shin, M.-Y. Lee, E.C. Dickey, T.N. Jackson, N.J. Podraza*, Penn State University

Hydrogenated amorphous and nanocrystalline silicon (a/nc-Si:H), germanium (a/nc-Ge:H), and their alloys have been used and continue to be assessed for use in uncooled infrared microbolometer applications. These materials may be deposited as uniform layers using equipment common to the manufacturing of displays and photovoltaics and are thus more amenable to manufacturing considerations than the ion beam deposited vanadium oxide films used in most commercial microbolometers. Real optimization of material in the a/nc-Si₁₋ₓGeₓ:H system for use in these devices requires a better understanding of the relationship between the key electrical properties of interest including resistivity (r), temperature coefficient of resistance (TCR), and the 1/f noise character as a function of the degree of order and composition of the films. Si₁₋ₓGeₓ:H thin films were deposited using plasma enhanced chemical vapor deposition using SiH₄, GeH₄, and H₂ at variable H₂- dilution. These films have been monitored using in situ real time spectroscopic ellipsometry (RTSE) over a spectral range from 0.75 to 5.15 eV during deposition to detect changes in the film thickness and optical properties in the form of the complex dielectric function spectra (e = e₁ + ie₂) as a function of deposition time. From the RTSE measurements and analysis it is possible determine the structure of the material as amorphous, nanocrystalline, or mixed-phase and track the evolution of nanocrystallinity as a depth profile into the film. Ex situ Fourier transform infrared spectroscopic ellipsometry measurements over a spectral range from 0.05 to 0.75 eV were also performed to augment the complex dielectric function spectra and study absorption features relating to bonding. For electrical measurements, contacts were deposited in an isolated transfer length pattern for measurement of resistivity and TCR, while resistors with different volumes were made for volume normalization of the 1/f noise measurements. The TCR was measured from 20ºC to 55ºC. This study explores to correlations between the electrical and optical properties of a-Si₁₋ₓGeₓ:H and nc-Si₁₋ₓGeₓ:H as functions of film processing conditions, resultant composition, and order. a-Si₁₋ₓGeₓ:H films were prepared as a function of germanium content and hydrogen dilution to identify the impact that germanium and improved order at higher hydrogen dilution conditions have on the electrical properties (r, TCR, 1/f noise). The impact on the electrical properties due to the incorporation of small fractions of nanocrystallites are explored using mixed-phase (a+nc)-Ge:H films with nanocrystallite profiles guided by depth profile studies.

5:20pm EL+AS+EM+MS+TF-ThA11 Roll-to-Roll Fabrication of Thin Film Si:H Solar Cells: Real Time Monitoring and Post Deposition Mapping by Spectroscopic Ellipsometry, *L.R. Dahal, Z. Huang, D. Attygalle, M.N. Sestak, C. Salupo, S.X. Marsillac, R.W. Collins*, University of Toledo

Real time spectroscopic ellipsometry (RTSE) has been used to monitor the roll-to-roll deposition of thin film Si:H n-i-p solar cells on flexible plastic substrates coated with a Ag/ZnO back-reflector. In this process, the RTSE monitoring position is located directly above the ZnO sputtering target (i.e., at the closest target-substrate separation). RTSE data collection is initiated before the plasma is ignited so that ZnO nucleation can be observed. The film thickness increases with time until a steady state is reached, after which the bulk layer thickness at the monitoring point is constant with time. This occurs when the elapsed deposition time equals the time required for the moving substrate to travel from the leading edge of the deposition zone to the monitoring point. Although a constant substrate speed is selected such that the final film thickness is achieved in the time required to move through the entire deposition zone, this speed does not allow study of film growth that occurs after the substrate passes the monitoring point. To solve this problem, the substrate speed is reduced only in the initial stage of growth such that the final film thickness of interest is reached at the monitoring point. In this way, RTSE can be used to analyze the entire layer on an initial length of the roll before the full length of the roll is processed. The thickness evolution of ZnO in the case of both normal and reduced

speeds shows good agreement with a simple inverse square variation of the deposition flux from the target to the flexible substrate.

After cell deposition, spectroscopic ellipsometry (SE) has also been applied for large area mapping of the completed 15 cm wide roll, at up to 1.5 m long sections at a time. Key information such as critical point, oscillator amplitudes, band gap energies, and widths have been extracted from which material density, composition, grain structure, disorder, and defect density can be determined. In this paper, optical mapping was applied for the intrinsic absorber layer in a full device a-Si:H solar cell structure. The results clearly show the degree to which thickness uniformity of the absorber layer depends on the gas flow and the electrode configuration. Also, by parameterizing the optical functions of the intrinsic absorber layer using single Lorentz oscillator modified by a low energy absorption cut-off, a map of its band gap and oscillator width can be deduced. Such an SE application is ideal for evaluation of uniformity in bulk thickness db, surface roughness thickness ds, index of refraction, and extinction coefficient (n, k); the critical parameters for fabricating uniform and high efficiency solar modules.

Graphene Focus Topic
Room: Brazos - Session GR+AS+TF+MI-ThA

Graphene: Surface Characterization
Moderator: P. Sutter, Brookhaven National Laboratory

2:00pm **GR+AS+TF+MI-ThA1 Scanning Tunneling Microscopy and Spectroscopy of Impurities on a Gated Graphene Device**, *R.T. Decker, V.W. Brar, M.H. Solowan, Y.C. Wang, A. Zettl, M.F. Crommie*, University of California Berkeley **INVITED**
Understanding the scattering properties of electrons in graphene is important for controlling the behavior of different graphene nanostructure-based devices. Here we report a scanning tunneling microscopy (STM) and spectroscopy (STS) study of impurities on a single monolayer of graphene. In our experiments the graphene is placed on a layer of insulating SiO_2 that sits above a doped silicon back-gate electrode. We will discuss our observations of the electronic local density of states of impurities, as well as how these properties respond to electrical gating of the graphene monolayer with respect to the silicon back-gate electrode.

In particular, we will show that the combination of the back-gate voltage and the STM tip-gating effect allows the controlled ionization of the impurity when the resonance sweeps through the Fermi energy. The influence of this induced Coulomb potential on the electrons in graphene in the vicinity of the impurity will be discussed.

2:40pm **GR+AS+TF+MI-ThA3 Graphene Defect States in a Magnetic Field Studied by Scanning Tunneling Spectroscopy**, *K.D. Kubista, D.L. Miller, M. Ruan, W.A. de Heer, P.N. First,* Georgia Institute of Technology, *G.M. Rutter, J.A. Stroscio*, National Institute of Standards and Technology
We present tunneling differential conductance (*dI/dV*) spectra and 2D conductance maps acquired over both positive and negative defects in magnetic fields up to 8 T. The measurements were performed on multilayer epitaxial graphene using scanning tunneling microscopy and spectroscopy at 4 K under ultrahigh vacuum conditions. Landau level drift states are found to follow the local potential (determined independently at near-zero magnetic field), but near a negatively-charged defect a bound (or quasibound) state originates from the $n = -1$ Landau Level. The defect state Stark shifts and finally ionizes under the influence of the STM tip electric field.

3:00pm **GR+AS+TF+MI-ThA4 Atomic-Scale Maps of Quantum Hall States in Epitaxial Graphene**, *D.L. Miller, K.D. Kubista,* Georgia Institute of Technology, *G.M. Rutter,* National Institute of Standards and Technology, *M. Ruan, W.A. de Heer, P.N. First,* Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology
When a perpendicular magnetic field is applied to a graphene sheet, the resulting eigenenergies (Landau Levels or LLs) have a nonlinear energy distribution that includes a four-fold degenerate zero-energy state (LL_0). Maps of the energy-resolved local density of states (LDOS) acquired via cryogenic scanning tunneling spectroscopy (STS) provide atomic-scale imaging of the LL spatial distribution. Focusing on LL_0, we use STS maps to image the *localized* and *extended* quantum Hall states. Unexpectedly, we find atomic-scale variations of the LDOS above a critical magnetic field. We attribute this to an energy gap in LL_0 and show how it depends on the local A-B lattice symmetry. The gap is observed only within patches of at least a few magnetic lengths in size, which forces the splitting to "turn off"

below the critical field. This behavior implies a breaking of the local sublattice symmetry imposed by moiré layer stacking.

3:40pm **GR+AS+TF+MI-ThA6 Imperfect Graphene: Point Defects, Edges, Dislocations and Grain Boundaries**, *O.V. Yazyev*, University of California, Berkeley **INVITED**

4:20pm **GR+AS+TF+MI-ThA8 Spectroscopic Ellipsometry for Thickness Measurement and Optical Dispersion Modeling of CVD-Grown Graphene**, *F.J. Nelson, V.K. Kamineni, A.C. Diebold*, The University at Albany-SUNY
Graphene has attracted much research over the past several years due to its electrical and mechanical properties. It is a prime candidate for electronic and optoelectronic devices, yet much of the research has utilized the exfoliation, or "scotch-tape" technique of sample preparation. More scalable growth methods have been investigated, such as the thermal decomposition of SiC, and the resulting graphene films have properties dependent on their fabrication parameters. One potentially scalable technique is that of hydrocarbon gas-based CVD onto metallic substrates. Here, we report on the ellipsometric measurement of Few-Layer-Graphene (FLG) grown on copper foils and subsequently transferred to a different substrate (i.e. glass). One of the challenges with development of a dispersion model for FLG is that the CVD graphene has many "grains" inside the measured area while previous reports of exfoliated graphene were done on single crystal samples. The work explores finding an average thickness, as well as the optical dispersion modeling, of the graphene layers on different substrates, such as SiO2/Si and glass slides.

**Spectroscopic Ellipsometry Focus Topic
Room: Southwest Exhibit Hall - Session
EL+AS+EM+MS+TF-ThP**

Spectroscopic Ellipsometry Focus Topic Poster Session

EL+AS+EM+MS+TF-ThP1 Temperature Dependence of the Dielectric Function of AlSb Measured by Spectroscopic Ellipsometry, *J.J. Yoon, Y.W. Jung, J.S. Byun, S.Y. Hwang, Y.D. Kim,* Kyung Hee University, Republic of Korea*, S.H. Shin, S.Y. Kim, J.D. Song,* Korea Institute of Science and Technology, Republic of Korea

AlSb is a promising material for applications in heterostructure devices such as long-wavelength detectors, quantum-well lasers, and laser diodes. However, to understand and properly design these devices, information about its electronic properties and its dielectric function $\varepsilon = \varepsilon_1 + i\varepsilon_2$ is needed. While room-temperature ε data for AlSb exist, very little information is available about its behavior at elevated temperatures. Here, we report pseudodielectric function data $\langle\varepsilon\rangle$ from 300 to 800 K and from 0.7 to 5.0 eV, determined by spectroscopic ellipsometry. The samples were 1.5 μm thick layers grown on GaAs (001) substrates by molecular beam epitaxy (MBE). This thickness significantly exceeds the critical value for AlSb, so the layers are fully relaxed. The MBE station features an integrated spectroscopic ellipsometer and strain-free windows, thereby allowing e data to be obtained without exposing the samples to air. For AlSb this is critical, because the removal of its oxides is not feasible owing to its reactivity. As a result of these precautions and the method by which these $\langle\varepsilon\rangle$ data were obtained, we consider them to be the most accurate representation of ε to date. We also analyzed these data for critical-point (CP) parameters by fitting numerically calculated second energy derivatives of to standard analytic CP lineshape expressions. A parametric model was used, which describes dielectric functions by a combination of energy-bounded polynomials and poles, and encodes information in terms of amplitudes, critical-point energies, and broadening parameters. The reconstructed spectra are in excellent agreement with the data. We use these parameters to obtain information about the individual oscillators, including phonon effects, and interpolate them to obtain an analytic representation of the dielectric response of AlSb as a function of temperature. We expect these results to be an important database supporting engineering design, device technologies, and in-situ monitoring and control of device fabrication.

EL+AS+EM+MS+TF-ThP2 Optical Properties and Humidity Effects on Thin Films of Micro Fibrillated Cellulose Studied by Spectroscopic Ellipsometry, *H. Arwin, **E. Antunez de Mayolo**,* Linköping University, Sweden*, M. Eita,* Royal Institute of Technology (KTH), Sweden*, H. Granberg,* Innventia Ab, Sweden*, L. Wågberg*, Royal Institute of Technology (KTH), Sweden

High quality micro fibrillated cellulose (MFC) prepared from wood fibers can be used to prepare thin films on solid substrates by a layer-by-layer deposition technique. In applications MFC layers can be used alone or as a constituent in functional coatings, where the MFC can make a significant contribution to mechanical properties of the coating. Examples of potential applications are sensor layers, decorative coatings or mirrors. Here the optical properties in terms of the refractive index of MFC are studied with *in situ* spectroscopic ellipsometry (SE) and the effects on thickness and index due to humidity are investigated.

Films of MFC and polyethyleneimine (PEI) in the thickness range 30 - 300 nm are deposited on silicon substrates. Such MFC/PEI samples are exposed to water vapor in nitrogen (0-90% RH) and the ellipsometric response are measured *in situ* in the spectral range 245 – 1700 nm at an angle of incidence of 70 degrees using a dual-rotating compensator ellipsometer. From the SE-data the MFC/PEI film thickness and layer index are modeled.

Due to water exposure, the thickness of an MFC/PEI film is found to increase up to 15% or more, whereas the refractive index decreases. The effects are fully reversible and the dynamics of these changes are monitored with SE and are discussed.

EL+AS+EM+MS+TF-ThP3 Spectroscopic Ellipsometry and X-ray Photoelectron Spectroscopy of La$_2$O$_3$ Thin Films Deposited by Reactive Magnetron Sputtering, *V. Atuchin,* Institute of Semiconductor Physics, Russia*, A.V. Kalinkin,* Boreskov Institute of Catalysis, Russia*, V.A. Kochubey, V.N. Kruchinin,* Institute of Semiconductor Physics, Russia*, R.S. Vemuri, C.V. Ramana*, University of Texas at El Paso

Lanthanum trioxide (La2O3) is one among the most promising high-*k* dielectric materials to replace SiO2 and Si3N4 in advanced metal-oxide-

semiconductor devices in gate stack. La2O3 can be prepared by various techniques but the film properties are strongly dependent on the fabrication conditions. Reactive magnetron sputtering deposition is widely used for the preparation of high quality transition multivalent metal oxide films with reproducible parameters and controlled thickness. The technique is preferred since it usually offers a high deposition rate for oxide films and a possibility to control the chemical composition of the film by reactive atmosphere in vacuum chamber. The aim of the present study is to understand the surface structure and evaluate the optical parameters of La2O3 films deposited on Si substrates by magnetron sputtering. La2O3 thin films were deposited onto Si(100) substrates in an argon/oxygen atmosphere using a high purity La target (99.9%). Structural parameters of the films were estimated by reflective high energy electron diffraction (RHEED) method at electron energy of 50 keV. All the films show no diffraction pattern indicating their amorphous nature in the near surface layers. Chemical state examined by the X-ray photoelectron spectroscopy (XPS), SPECS device, monochromatic Al Ka radiation (1486.6 eV) before and after Ar+ (2.5 keV, 2 min) sputtering indicates the stoichiometric film formation. Chemical nature of the species was identified with using binding energy (BE) difference parameter DLa = BE (La 3d5/2) - BE (O 1s) [1]. Optical parameters of the films were measured with spectroscopic ellipsometry (SE) using a Spectroscan ellipsometer in the spectral range of 250 nm < l < 1100 nm at the incidence angle of 70°. The La2O3 films with thickness 500-850 nm were transparent over the spectral range and dispersion relations of refractive index *n* were well derived using a model of (air)/(single homogeneous layer)/(Si substrate). The curves *n*(l) were approximated by Caushy polynomials. Good relation between experimental points and theoretical curves confirms applicability of this simple model for the films. The optical parameters of La2O3 defined with SE are related to film bulk and are insensitive to top surface effects induced by hydration or carbonate formation. These parameters will be used as a basis for SE evaluation of nanometric lanthanum oxide films with thickness below 10 nm.

1.V.V. Atuchin, T.A. Gavrilova, J.-C. Grivel, V.G. Kesler, Electronic structure of layered ferroelectric high-k titanate La2Ti2O7, J. Phys. D: Appl. Phys. 42 (2009) 035305.

EL+AS+EM+MS+TF-ThP4 Analysis of Anomalous Film Growth when Yttrium Oxide Thin Films are Exposed to 7.2eV Light, *D. Mortensen, D.D. Allred*, Brigham Young University

We have recently found that exposure of reactively sputtered yttrium oxide thin films to 7.2 eV photons in air produces a dramatic (factor of 4) increase in the films' thickness. This result was completely unexpected, Y2O3 is exceptional stable, and demanded further investigation. This is particularly important since yttria and neighboring metal oxides such as ZrO2 have been considered, and HfO2 is being used, as components in gate oxides for silicon devices. The excimer lamp used for the study was of the type used in cleaning the surfaces of silicon wafers in the semiconductor industry. It is vital to understand how metal oxides might swell during cleaning.

We have experimentally observed the following:

1. The film-thickness increase is linear with exposure time up to a point.

2. Over a factor of four increase in film thicknesses, as measured by spectroscopic ellipsometry, has been observed. E.g., film which was about 20 nm thick as deposited reached a thickness of about 100nm.

3. When the yttrium oxide sample is placed in a furnace the changes rendered to the yttrium oxide sample are reversed.

4. A film placed in a plasma cleaner does not show this increase.

5. These effects are noticeably absent under the same conditions for a silicon wafer.

6. The refractive index of the film decreased with exposure time, suggesting the film could becoming more porous, though effective media optical models were unsuccessful in modeling the optical properties.

In addition to ellipsometry the films were studied by XPS and STEM.

EL+AS+EM+MS+TF-ThP5 In-Situ Spectroscopic Ellipsometry of Lithium Ion Intercalation in GLAD Three-Dimensional Nanostructured Thin Films, *E. Montgomery*, *M. Schubert, E.B. Schubert, T. Hofmann, D. Schmidt,* University of Nebraska - Lincoln*, R.A. May,* University of Texas at Austin

Lithium intercalation in thin nanostructured and bulk films from metals and semiconductors has been studied using in-situ spectroscopic ellipsometry. Nanostructured thin films have a large surface area, and the stress caused by the intercalation of lithium is reduced in comparison to continuous films. The films are deposited using electron beam evaporation at a glancing angle or Glancing Angle Deposition (GLAD).

The charge capacity of the films can be observed as a change of index of refraction using ellipsometry. We will study intercalation as a function of structure geometry in chiral and achiral 3D GLAD thin films deposited from different metals onto silicon and other dielectric substrates. We report the anisotropic dielectric functions of the 3D nanostructures and their changes as a function of intercalation time and period.

EL+AS+EM+MS+TF-ThP6 Multi Phase Model Generation of Reflection Anisotropy Spectra of Copper Phthalocyanine Films on Vicinal Silicon Substrates, *F. Seidel*, *L. Ding, O.D. Gordan, D.R.T. Zahn,* Chemnitz University of Technology, Germany

In this work the in-plane anisotropy of copper phthalocyanine (CuPc) thin films grown on vicinal silicon substrates is explained by simulating Reflection Anisotropy Spectroscopy (RAS). In RAS the complex difference in reflection along two perpendicular directions is measured at an incidence angle close to 0°. While RAS has strong similarities with another polarisation related measurement technique, Spectroscopic Ellipsometry (SE), simulations of RA spectra using a similar mathematical formalism like in SE is not common.

One difference is that in SE the measurements are usually performed at an incidence angle close to the Brewster angle, where the difference between s and p reflected polarisation is maximal. However due to the similarities between the two techniques the evaluation of RA spectra can be performed in a similar way like for SE after some simple mathematical transformations. This in particularly useful when thickness induced interference can lead to incorrect interpretations of RA spectra. Therefore in this work we show that the RA spectra evaluation of CuPc layer with increasing thickness is mainly given by the optical interference effect and not by a change in the optical anisotropy of the film.

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