

# Sunday Afternoon, October 30, 2011

## Biomaterials Plenary Session

Room: 108 - Session BP-SuA

### Challenges in Biomaterials Analysis

**Moderator:** L. Gamble, University of Washington

3:00pm **BP-SuA1 Wants, Needs, and Challenges in Biomedical Surface Analysis, D.G. Castner**, University of Washington **INVITED**

Biomedical surface analysis has undergone significant and numerous advances in the past 30 years in terms of improved instrumentation, introduction of new techniques, development of sophisticated data analysis methods, and the increasing complexity of samples analyzed. Comprehensive analysis of surfaces and surface immobilized biomolecules (peptides, proteins, DNA, etc.) with modern surface analysis instrumentation provides an unprecedented level of detail about the immobilization process and the structure of the immobilized biomolecules. Results from x-ray photoelectron spectroscopy (XPS or ESCA), time-of-flight secondary ion mass spectrometry (ToF-SIMS), near edge x-ray absorption fine structure (NEXAFS), surface plasmon resonance (SPR) biosensing, atomic force microscopy, and sum frequency generation (SFG) vibrational spectroscopy provide important information about the attachment, orientation, conformation, etc. of biomolecules. However, even with the advances that have been achieved with these powerful surface analysis techniques, there still remains many significant challenges for biomedical surface analysis. These include characterizing the surface chemistry and structure of nanoparticles, determining the structure of protein bound to surfaces, and maintaining biomolecules and materials in a biological relevant state when using ultra-high vacuum based analysis techniques.

This talk will discuss the current challenges in biomedical surface analysis and what is being done to address them. Also discussed will be the role of well-defined standards to develop new biomedical surface analysis methods for characterizing more complex, biological relevant samples.

3:40pm **BP-SuA3 Depth Profiling and 3D Analysis of Organic Surfaces, A.G. Shard**, National Physical Laboratory, UK **INVITED**

Cluster ion impacts have been shown to sputter organic materials, whilst imparting low levels of damage to the freshly exposed surface. When coupled with a surface analytical technique, such as SIMS or XPS, it is possible to generate depth profiles with truly molecular information. Concurrent 2D spectroscopic imaging enables a three dimensional reconstruction of molecular distributions. This offers enormous potential for the label-free and multiplexed imaging of biological materials and medical devices.

The mechanism of cluster ion beam sputtering has been established over the past ten years and the most important factor that permits organic depth profiling is the large sputtering yield of organic material following a cluster ion impact. This is typically of the order of 100 nm<sup>3</sup> of material per individual impact. However it has been shown that, for many materials, the sputtering yield changes as the cluster ion dose increases and therefore the interpretation of organic depth profiling data is, in general, not trivial. Additionally, this change in sputtering yield is often associated with sputter-induced roughening with a concurrent degradation of depth resolution. Recently, there has been a growing emphasis on the development of methods by which a wider range of materials can be depth profiled and a constant sputtering yield maintained. The most significant advances have been the use of sample cooling, low ion beam incidence angles and sample rotation. Large argon clusters appear to offer significant improvements over traditional cluster beams, such as C<sub>60</sub> in these regards.

The reliability of organic depth profiling was tested recently in two VAMAS interlaboratory studies. Results from these studies highlight the rapid developments that have recently been made. The application of this technique to medical devices and biological materials will be reviewed and the remaining challenges described.

4:20pm **BP-SuA5 Nanoscale Surface Analysis of Living Cells using Atomic Force Microscopy, Y.F. Dufrene**, Université catholique de Louvain, Belgium **INVITED**

The emerging new field of "live-cell nanoscopy" has revolutionized the way biologists explore the living cell to molecular resolution. Whereas far-field fluorescence nanoscopy enables to study the nanoscale localization and dynamics of biomolecules in cells, recent developments in atomic force microscopy (AFM) techniques offer unprecedented opportunities for imaging the supramolecular organization of cell surfaces, and for probing

the functional properties and interactions of their molecular machineries. In the past few years, AFM-based nanoscopy has enabled key breakthroughs in cell biology, including deciphering the nanoscale architecture of cell surfaces and their remodelling upon changing the cells functional state, understanding cellular mechanics and its functional implications, quantifying cell adhesion forces contributing to processes like tissue development and bacterial infection, unravelling the molecular elasticity of cellular proteins such as sensors and adhesion molecules, and elucidating how cells reassemble membrane receptors into nanodomains and modulate their functional state. In this talk, I will provide a survey of the recent work we have done using the AFM multifunctional toolbox, emphasizing its potential for understanding cell surface properties and interactions on the nanoscale.

#### References

- Nat. Chem. Biol., 5 (2009), 857-862.
- Nat. Commun., 1:27 (2010).
- Proc. Natl. Acad. Sci. USA, 107 (2010), 20744-20749.
- Nat. Methods, 8 (2011), 123-127.

5:00pm **BP-SuA7 AVS 2011 Biointerphases Lecture - Tissue Engineering and Surface Science: 2D to 3D, Dry to Wet, Dead to Living and the Challenges to the Instrumentation, B.D. Ratner\***, University of Washington Engineered Biomaterials **INVITED**

The biointerface and related surface science ideas have had profound impact on biomaterials science since at least the 1960's. In the 21<sup>st</sup> century there is much discussion of tissue engineering, clearly a "3-D" phenomenon. This talk will review some history of the biointerface, illustrate modern trends, and show how biointerface ideas can be applied to tissue engineering and 3-D scaffolds. Techniques such as electron spectroscopy for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS) will be featured. SIMS has proven to be powerful for cell identification in culture dishes and for the analysis of decellularized extracellular matrix scaffolds. SIMS also provides much information on synthetic scaffold materials. There are now profound challenges in interpretation of complex spectra and in gleaning useful, biomedically relevant information from complex data sets. Finally, this talk will discuss healing, biointegration and regeneration, particularly in the context of new scaffolds made by a sphere-templating process.

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\* AVS 2011 Biointerphases Lecture

# Monday Morning, October 31, 2011

Applied Surface Science Division

Room: 102 - Session AS-MoM

## Quantitative Surface Chemical Analysis and Technique Development - Part I

Moderator: I.S. Gilmore, National Physical Laboratory, UK

8:20am **AS-MoM1 Characterization of Nano-structures from Analysis of the XPS Background: Automation and 3D-imaging.** *S. Tougaard*, University of Southern Denmark **INVITED**

The XPS peak intensity and its background of inelastically scattered electrons varies strongly with the depth distribution of atoms. This phenomenon is the basis for a widely used method for nano-structure analysis.<sup>1</sup> With the rapid increase in the application of XPS, there is a growing need for automated XPS analysis. To meet this demand, a modified simpler and less accurate algorithm, which however is suitable for automation was developed.<sup>2</sup> For each XPS peak, this algorithm determines just two numbers: the total amount of atoms within the outermost ~ 10 nm and the approximate depth of the atoms. The validity of the algorithm was demonstrated experimentally by comparison to more elaborate quantification methods.<sup>2</sup> The algorithm is thus of interest for automated XPS analysis. Another application of the algorithm is in XPS imaging, where thousands of spectra must be analyzed. Here automatic data-handling procedures are crucial. Software that can automatically analyze thousands of spectra corresponding to the situation in XPS imaging is now being developed. The method produces nondestructively a 3-D image of the surface with nanometer depth resolution. The practical applicability of this to XPS imaging was recently demonstrated.<sup>3,4</sup>

In ref<sup>3</sup> the algorithms ability to produce images of Ag taken from a series of samples with increasing thicknesses of plasma patterned Octadiene (2, 4, 6 and 8nm) on Ag substrates was demonstrated. The obtained images of the amount of Ag atoms in the outermost few nano-meters were in good agreement with the nominal thicknesses. Produced images of atoms at different depths clearly proved the potentials of the method for quantitative and nondestructive 3-D characterization of nano-structures. Spectral noise is a major limitation in imaging because the time allowed to acquire the spectrum at each pixel is typically ~1 sec. Different procedures for noise reduction were studied in ref<sup>3</sup> and principal component analysis (PCA) was found to significantly improve the 3D images of a thermally patterned oxidized silicon where detailed 3-D images of the Si, O, and C atoms were determined on the nano-meter depth scale.

In the talk we will summarize the technique and discuss its limitations and potentials for both automation of conventional XPS data analysis and for 3D XPS imaging.

<sup>1</sup> S. Tougaard, Surf. Interf. Anal. 26 (1998) 249

<sup>2</sup> S. Tougaard, J. Vac. Sci. Technol., A21 (2003) 1081; A23(2005) 741

<sup>3</sup> S. Hajati, S. Coultas, C. Blomfield and S. Tougaard, Surf. Interf. Anal. 40 (2008) 688

<sup>4</sup> S. Hajati, J. Walton, N. Fairley, and S. Tougaard, Surf. Sci. 602 (2008) 3064

9:00am **AS-MoM3 Characterization of Model Gradient Inorganic Thin Films with XPS Spectral Modeling.** *L. Lohstreter*, Medtronic, Inc, *R. Sanderson, J. Dahn*, Dalhousie University, Canada

Information about the layer structure of surfaces at the angstrom level can be probed through X-ray Photoelectron Spectroscopy (XPS) by analyzing the structure of the entire spectrum, including the inelastic background. Model samples were prepared through a unique magnetron sputtering system to create thin film gradients ranging from two angstroms to hundreds of angstroms thick across a distance of seven centimeters. The system studied consisted of a titania wedge on a gold substrate. The samples were characterized using Variable Angle Spectroscopic Ellipsometry (VASE) to measure the thickness of the wedge along the sample at many points along the gradient. The thickness values from the XPS and VASE modeling were shown to have excellent linearity from two angstroms until the XPS photoelectron peak was extinguished. The effective attenuation lengths of the titania at the kinetic energies of the various gold photoelectron peaks were also measured and compared to theoretical values for inelastic mean free path. The values were within 29% of each other.

9:20am **AS-MoM4 Corrections for Backscattering Effects in Quantitative Auger Analyses.** *A. Jablonski*, Polish Academy of Sciences, Poland, *C.J. Powell*, National Institute of Standards and Technology

The backscattering factor (BF) has long been recognized as an important matrix-correction factor for quantitative AES. The BF definition ("fractional increase in the Auger current due to backscattered electrons" [1]) has been shown to be unsatisfactory since the "fractional increase" can be negative at low primary energies and more grazing-incidence of the primary electrons [2]. ISO/TC 201 is considering the definition of a new term, the backscattering correction factor (BCF), as a "factor equal to the ratio of the total Auger-electron current arising from ionizations in the sample caused by both the primary electrons and the backscattered electrons to the Auger-electron current arising directly from the primary electrons." NIST recently released a new BCF Database [3] for AES. This database provides BCFs from Monte Carlo simulations for two models, a simplified model based on the previous BF definition which is relatively rapid and an advanced model based on the proposed BCF definition which is more accurate but slower. BCFs can be determined for a solid of arbitrary composition, a user-specified instrumental configuration, and primary energies up to 30 keV.

Examples will be given of the dependence of the BCF for Pd M<sub>5</sub>N<sub>45</sub>N<sub>45</sub> Auger electrons on various instrumental conditions (primary energy, primary-beam angle of incidence ( $\theta_0$ ), and analyzer acceptance solid angle) [4]. BCFs calculated from the advanced model of electron transport in the surface region of the Pd sample varied weakly with analyzer half-cone angle for  $\theta_0 = 0^\circ$  but more strongly for  $\theta_0 = 80^\circ$  where there were BCF differences varying between 19% at a primary energy of 1 keV and 6% at a primary energy of 5 keV. These BCF differences are due partly to variations of the density of inner-shell ionizations within the information depth for the detected Auger electrons. The latter variations are responsible for differences larger than 10% between BCFs from the widely used simplified BCF model and those from the more accurate advanced model for primary energies less than about 5 keV for  $\theta_0 = 80^\circ$ . These and other BCF differences indicate that the simplified model can provide only approximate BCF values. In addition, the simplified model does not provide any BCF dependence on Auger-electron emission angle or analyzer acceptance angle. Comparisons will also be made with measured BCFs for elemental solids.

[1] ASTM E 673-03, "Standard Terminology Relating to Surface Analysis," in Annual Book of ASTM Standards, Vol. 3.06, 2010, p. 655.

[2] A. Jablonski, Surf. Science 499, 219 (2002).

[3] <http://www.nist.gov/srd/nist154.cfm>.

[4] A. Jablonski and C. J. Powell, Surf. Science 604, 1928 (2010).

9:40am **AS-MoM5 Effect of Monochromator X-ray Bragg Reflection on Photoelectric Cross Section.** *A. Herrera-Gomez*, CINVESTAV-Unidad Queretaro, Mexico

The photoelectric differential cross section plays a fundamental role for assessing the relative concentration of the various elements present within the XPS probing depth. Accounting for the different issues affecting the cross section is paramount not only for quantitative chemical studies (including angle-resolved XPS) but also for a proper comparison between the results obtained with different XPS tools, or in the same tool but with different X-ray sources. In XPS experiments employing monochromatized light, the X-ray Bragg reflection undergone by the beam at the monochromator crystal causes a partial polarization of the X-rays. The photoelectric cross section is affected since it depends on the angle between the electric field vector and the direction of the escaping electrons. An expression for the photoelectric differential cross section is presented that accounts for the effect of the monochromator and of the geometrical configuration of the XPS tool. The correction is as large as 9% for s-orbitals and reduces to up to 5% for orbitals with  $\beta \sim 1$ . The differences are directly related to the beta factor within the dipole approximation, which is the first order treatment of photoemission; i.e., they are not due to higher order quadruple terms.

10:00am **AS-MoM6 An XPS Investigation of CdS Based Photoresistor During Operation.** *S. Suzer, H. Sezen*, Bilkent University, Turkey

We have recently developed a technique for recording the shifts in the positions of the XPS peaks in response to different waveforms of electrical and/or optical stimuli for probing the dynamics of the developed electrical potentials originating from intrinsic or extrinsic (like doping) properties of semiconductive materials such as charging/discharging, photoconductivity, surface photovoltage, band-bending/flattening/inversion, etc.<sup>1-6</sup> We have also shown that fast data acquisition (in the snapshot mode) and laterally spatial resolved XPS analysis (an area mapping mode) helps us to compare and

align extracted electrical behaviors and chemical information from the sample. For a better understanding of a realistic performance (or failure) of a device during operation, we have extended our measurements to a CdS based photoresistor, where we have mapped the position of the Cd3d peak over an area of 5 mm x 5mm while the device is under operation without and under photoillumination. This method allows us to detect defects and malfunctioning sites/domains. We will present our methodology with experimental results and an electrical circuit model.

- (1) Sezen H., Suzer, S. *Surface Science*, **2010**, 604, L59.
- (2) Suzer, S., Sezen, H., Ertas, G., Dâna, A. *Journal of Electron Spectroscopy and Related Phenomena* **2010**, 176, 52.
- (3) Sezen, H., Ertas, G., Suzer, S. *Journal of Electron Spectroscopy and Related Phenomena*, **2010**, 178-9, 373.
- (4) Sezen H., Suzer, S. *Journal of Vacuum Science and Technology A*, **2010**, 28, 639.
- (5) Sezen, H., Ozbay, E., Aktas, O., Suzer, S. *Applied Physics Letters* **2011**, 98, 111901.
- (6) Sezen, H., Suzer, S. *Journal of Spectroscopy and Dynamics* (in press).

10:40am **AS-MoM8 Coronene Ion Bombardment Effects in the Quantitative Analysis of Polymeric Materials by XPS**, *G.E. Hammer, L.J. Gamble, D.G. Castner*, University of Washington

XPS has long been a primary technique for the analysis of material surfaces, providing quantitative analysis of elemental atomic concentrations and chemical bonding states. When combined with ion sputter etching, it has provided a similar level of detail in depth profiling of metals, semiconductors, and inorganic compounds; however, the damage produced by ion bombardment precluded the depth profiling of organic and polymeric specimens. More recently it has been shown that sputter etching by carbon cluster ions significantly reduces the apparent damage to such materials, presumably the result of a combination of a reduced damage layer thickness and efficient removal of the damaged material. In this work we have used a coronene ( $C_{24}H_{12}^+$ ) ion source to sputter etch a series of organic compounds and polymers, including trehalose, poly(amide), poly(glycolic acid), poly(lactic acid), poly(ethylene glycol), poly(methyl methacrylate), poly(acrylonitrile), poly(ethylene terephthalate), poly(vinyl chloride), and poly(tetrafluoroethylene). Specimens were sputtered to a steady-state condition and analyzed by XPS. Elemental composition and chemical bonding were compared to the original surface and the theoretical values. These data will be used to refine our understanding of cluster ion bombardment effects in polymers, and to interpret data from the analysis of future materials and devices.

11:00am **AS-MoM9 Using A C60 Ion Source For Routine Surface Chemical Analyses**, *W. Stickle, M.D. Johnson, D.K. Bilich*, HP ADL Corvallis, *C. Knutson, W. Wang, W. Cowell*, Oregon State University

$C60^+$  ion sources are becoming one of the routinely used tools in the surface chemical analysis laboratory. While finding early acceptance and utility in the TOF SIMS community because of its direct applicability to organic systems, the  $C60$  ion source is now a standard option for photoelectron spectroscopy tools. Routine use of this ion source requires characterization and understanding of the surface that is being created during the ion milling process. Such characterizations include the shape and roughness of the resulting surface, changes in chemistry of the surface created by the ion milling process and changes in the mechanical characteristics of the surface that might influence the interpretation of the surface analytical results. Full characterization requires the preparation of standards and also validation of the measurements. The characterization of the application of the  $C60$  ion source for a variety of common polymers such as PMMA, SU8 and polycarbonate are discussed. Further, anticipating the examination of mixed mode systems, the application of the  $C60^+$  source for the characterization of inorganic materials such as titania, hafnia and alumina multilayered structures as well as metal-metal oxide layered structures is presented where sputter induced chemistry from the  $C60^+$  source is observed.

11:20am **AS-MoM10 Large Area Quantitative XPS Imaging for Small Feature Compositional Screening**, *S.J. Coultas, C.J. Blomfield, S.J. Hutton, A.J. Roberts*, Kratos Analytical Ltd, UK, *D.J. Surman*, Kratos Analytical Inc.

Many technologically important devices require nanometre level chemical characterisation over areas of several square mm, or even cm, for applications such as coating continuity and integrity or contamination monitoring.

The traditional approach when employing XPS for this application has been to acquire a number of small area spectra at different points. The advent of quantitative parallel XPS imaging introduced the possibility of faster

acquisition times and higher spatial resolution than the traditional small XPS probe approach.

Here we present an alternative approach whereby multiple features are simultaneously analysed over a large area using XPS imaging. Acquisition conditions and post acquisition data treatment to optimise this approach on a range of samples will be discussed

This approach provides both a faster and more easily interpreted graphical method for multiple feature analysis.

We present examples of this approach on a variety of samples.

11:40am **AS-MoM11 A New Type of Detector for Dynamic XPS Measurements**, *K. Winkler, P. Baumann, B. Kroemker, G. Pruemper, A. Feltz*, Omicron NanoTechnology, Tautausstein, Germany

Real time observation of fast processes occurring in a time window of a few milliseconds to a few minutes have been always difficult to observe by x-ray excited photoemission (XPS) studies under laboratory conditions. However the demand to understand the chemistry of surface processes e.g. during heating processes, electro migration and diffusion is of high relevance in various research fields.

In this contribution we will report on first results of a new multi-anode detector concept with 128 individual anodes, preamplifiers and counters. It has the capability to allow for quantitative XPS studies on fast time scales with good signal to noise ratio excited with a monochromated Al K $\alpha$  laboratory source. The detector can be operated in snapshot XPS mode. This mode allows recording an energy window in the spectrum versus time with high repetition-rates and good energy resolution, e.g. a 15 eV detectable energy window with an approximate energy resolution of 0.5 eV.

As an early application we report on results of removing an in-situ grown SiO $_2$  layer on a Si substrate. The measurement was made during a sample temperature ramp from 600 to 900 degree Celsius within a time frame of one hour. The target of the experiment was to analyze the time window in which the oxide was removed.

Snapshot spectra have been recorded with an acquisition time of 0.5 seconds per spectrum to follow the evolution of the subcomponents Si $4+$  to Si $0$  during the heating process of the Silicon. The snapshot series with >5000 spectra shows the evolution of the peak versus time. The complete removal of the oxide occurred at a very small temperature window around 850°C. A closer look into the data revealed that the removal of the oxide from the silicon took place in about 2.5 minutes. Within this transition time 300 spectra have been recorded.

**In Situ Spectroscopy and Microscopy Focus Topic**  
**Room: 106 - Session IS+AS+SS-MoM**

**In Situ Studies of Catalysis and Gas-Solid Reactions**  
**Moderator: G. Rijnders**, University of Twente, the Netherlands

8:20am **IS+AS+SS-MoM1 In Situ X-ray Studies of Model and Real Catalysts: Bridging the Complexity Gap**, *A.I. Frenkel*, Yeshiva University **INVITED**

In the last decade, there was a surge in advanced characterization methods to study catalytic materials at work. Most notable innovations in synchrotron-based techniques include the coupling of in situ/operando x-ray absorption and scattering methods to vibrational spectroscopies, empowered by improved time and energy resolutions. For example, in situ XAFS-XRD combination enables complementary studies of short and long range order in the same system, a great tool when multiple spatial dimensions evolve in a certain process, such as: modifications of both the catalyst and the support during catalytic reaction, the nucleation and growth of a nano-catalyst, oxidation/reduction of a bulk oxide. Combining in situ XAS or XRD with infrared or Raman spectroscopy is critical for understanding how the structural and electronic properties of a catalyst relate to its reactivity.

Although these are important new improvements in the way we currently study, and understand, processes in nanomaterials, they are done by methods that are not sensitive to local fluctuations in size, shape, structure of nanomaterials, that are present even in well-defined, model catalysts. Thus, in addition to the ensemble averaging that these and other commonly used methods provide, local information, such as one provided by electron microscopy, is needed. In this talk, I will focus on the new efforts in combining the local and average information by coupling the in situ x-ray

absorption spectroscopy to in situ environmental transmission electron microscopy (E-TEM) for in situ investigations. Such experiments, done in two separate facilities (NSLS and CFN) at Brookhaven National Laboratory, revealed anomalous, mesoscopic phenomena in the electronic, structural and thermal properties of supported Pt nanoparticles. These systems have long been excellent model systems in catalysis research, yet, at a closer look, as our in situ measurements demonstrated, they turned out to be much more unstable and complex than previously perceived. These clusters exhibited unique physical properties, such as negative thermal expansion, increase in the Debye temperature, broad amorphous-to-crystalline transition zone, large surface strain, as well as charge exchange with support and adsorbates.

I will review recent works showing how such complex behaviors can be, in the case of Pt on g-alumina and carbon supports, theoretically understood by separately studying the effects of their size, shape, support and adsorbates.

**9:00am IS+AS+SS-MoM3 Communicating Nanostructures: Spillover Processes Studied on Ceria-supported Platinum Nanoparticles, M. Happel, Friedrich-Alexander-Univ., Germany, Y. Lykhach, T. Staudt, Friedrich-Alexander-Univ., Germany, N. Tsud, Charles Univ., Czech Republic, T. Skála, K.C. Prince, Sincrotrone Trieste, Italy, V. Matolin, Charles Univ., Czech Republic, A. Migani, Univ. de Barcelona, Spain, G.P. Petrova, Univ. of Sofia, Bulgaria, A. Bruix, F. Illas, K.M. Neyman, Univ. de Barcelona, Spain, G.N. Vayssilov, Univ. of Sofia, Bulgaria, J. Libuda, Friedrich-Alexander-Univ. Erlangen-Nuremberg, Germany**

Ceria-based catalysts are technologically important for various applications, including automotive catalysis, SO<sub>x</sub> scrubbers, and hydrocarbon transformation reactions. The complex surface chemistry and reaction kinetics in these systems are assumed to be strongly influenced by so-called metal-oxide (MO) interactions. We use a surface science-based model approach to obtain detailed insight into the origins of such effects at the microscopic level.

The model catalysts are based on ordered CeO<sub>2</sub>(111) films on Cu(111), on which noble metal nanoparticles (e.g. Pt) are grown by PVD under UHV conditions. The growth and geometric structure of the model catalysts are characterized by STM. Adsorption and reaction are followed by XPS, synchrotron radiation photoelectron spectroscopy (SR-PES), IRAS, and molecular beam (MB) methods, in combination with DFT calculations. Resonant PES (RPES) is used to monitor the changes in the cerium oxidation state with high sensitivity.

Two types of MO interaction are identified, electron transfer from the Pt nanoparticle to the support, and oxygen transfer (spillover) from ceria to Pt. Whereas electron transfer occurs on ceria supports irrespective of their morphology, oxygen transfer shows a pronounced structure dependency, i.e. it requires the presence of nanostructured ceria aggregates in close contact with Pt.[1]

Not only oxygen spillover, which is a key step in oxidative-self cleaning of carbon-poisoned catalysts, but also spillover and reverse-spillover of hydrogen and hydrocarbon fragments can be followed in detail by RPES. A particularly complex behavior is expected for SO<sub>x</sub>, for which strong MO effects and spillover have been suggested in previous studies on powder catalysts. On the Pt-free model support we identify different sulfur species forming upon SO<sub>2</sub> exposure even at 150 K (sulfites, atomic sulfur, and potentially sulfates), formed via different adsorption, decomposition and disproportionation pathways. At higher temperature, these species transform into a bulk-like cerium oxysulfide. For interpretation of the sulfur-chemistry on Pt/CeO<sub>2</sub>, reference experiments on Pt(111) were performed and numerous SO<sub>x</sub> species were identified by IRAS and SR-PES. RPES for SO<sub>2</sub> adsorption on Pt/CeO<sub>2</sub> provides direct evidence for spillover of SO<sub>x</sub> to the Pt nanoparticles above 300 K. Between 300 K and 600 K Pt acts as a "sulfur-collector", before at even higher temperatures sulfur is finally transformed into a cerium oxysulfide species.

[1] G. Vayssilov, Y. Lykhach, A. Migani, T. Staudt, G.P. Petrova, N. Tsud, T. Skála, A. Bruix, F. Illas, K.C. Prince, V. Matolin, K.M. Neyman, J. Libuda, *Nat. Mater.* **2011**, *10*, 310.

**9:20am IS+AS+SS-MoM4 HPXPS Study of the Oxidation of 10 nm PdAg Nanoparticles, S. Blomberg, J. Gustafson, N.M. Martin, M.E. Messing, K. Deppert, J.N. Andersen, Lund University, Sweden, L.E. Walle, A. Borg, Norwegian University of Science and Technology, Norway, H. Grönbeck, Chalmers University of Technology, Sweden, M.E. Grass, Z. Liu, Lawrence Berkeley National Laboratory, E. Lundgren, Lund University, Sweden**

Due to the economic and environmental rewards, one goal in catalysis related research is to create cheaper catalysts. One way to realize this is to dilute the more expensive active catalyst material with a less costly one. This requires that the active material stays at the surface. This could be achieved by using a material which is less prone to interact with the reactant

gases, such as a noble metal. In most catalysts, the active material is dispersed in a high area complex oxide support as nanoparticles. In order to maintain the high activity, it would be necessary to ensure that the active material is at the surface of the nanoparticle.

In the present contribution we report on our initial findings from attempts to produce PdAg alloy particles using an aerosol deposition technique [1]. The particles have a diameter of 10 nm distributed over a SiO<sub>x</sub> wafer. The samples was characterized by high pressure XPS, SEM and TEM as was done previously for aerosol Pd particles [2,3]. By comparing to XPS data from a single crystal Pd<sub>75</sub>Ag<sub>25</sub>(100) and from The X-ray Energy Dispersive Spectroscopy (XEDS) analysis we show that the PdAg particles have a similar alloy composition.

The *in-situ* high pressure XPS data from the 10 nm PdAg particles demonstrates that the Pd segregates to the surface in an oxygen rich environment and that the core of the particles are rich in Ag. Although a thin PdOx shell is formed, bulk oxidation is inhibited. The limited oxide formation is promising for the full oxidation of methane, since recent investigations [4] suggest that the PdO is less active for methane oxidation than the metallic Pd.

[1] M. E. Messing, K. A. Dick, L. R. Wallenberg, K. Deppert, *Gold Bull.* **42** (2009) 20.

[2] M. E. Messing *et al*, *J. Phys. Chem. C.* **114** (2010) 9257.

[3] R. Westerström *et al*, *Phys. Rev. B.* **83**, (2011) 115440.

[4] A. Hellman *et al.*, submitted.

**9:40am IS+AS+SS-MoM5 New Assignment for Ag(III) from In Situ XPS of Highly Oxidized Silver Films, T.C. Kaspar, T. Droubay, S.A. Chambers, Pacific Northwest National Laboratory, P.S. Bagus, University of North Texas**

For decades, it has been a goal to elucidate the mechanisms behind the unique chemistry of both oxygen-exposed silver metal and silver oxides. Silver compounds in bulk, thin film, and nanoparticle form are widely investigated for applications including industrially-relevant catalysis, electrochemistry, transparent conducting oxides, and antimicrobial coatings. Determining the chemical state of both silver and oxygen is critical to developing a mechanistic understanding of the remarkable properties of these materials. *Ex situ* x-ray photoelectron spectroscopy (XPS) has been applied, starting in the 1970's, to determine the chemical state of Ag in various silver metal and silver oxide compounds. In contrast to most elements, Ag<sup>x+</sup> (x>0) cations exhibit a negative binding energy (BE) shift relative to metallic Ag(0); thus, the lowest XPS core level binding energy observed for the Ag 3d peak, 367.3 eV, has been assigned to Ag(III) in AgO [Ag(I)Ag(III)O<sub>2</sub>]. However, the XPS analysis has been hindered by the ease with which silver oxides form carbonate species upon atmospheric exposure, as well as the instability of silver oxides in vacuum. In this work, silver oxide films have been formed under very oxidizing conditions, by molecular beam epitaxy (MBE) deposition of silver metal in the presence of activated oxygen. *In situ* XPS was then collected in an appended chamber. For the most highly oxidizing deposition conditions, a substantially lower BE, 366.8 eV, was found for the Ag 3d peak, with an associated satellite located at 368.2 eV. This oxide species proved unstable in vacuum over several days, but could be recovered by further exposure to activated oxygen. Based on the decomposition behavior of the Ag 3d and O 1s spectra, the low BE species was assigned as Ag(III), while the previous peak position for Ag(III) was re-assigned as Ag(I). These assignments are supported in part by electronic structure calculations predicting the photoemission spectra of Ag(III). The combination of highly oxidizing deposition conditions and *in situ* characterization allowed identification of the true Ag(III) XPS spectrum for the first time.[1]

[1] T.C. Kaspar, T. Droubay, S.A. Chambers, and P.S. Bagus. *J. Phys. Chem. C* **114** 21562 (2010).

**10:00am IS+AS+SS-MoM6 The Oxidation of Methane Over Pd, A. Hellman, Chalmers Univ. of Tech., Sweden, A. Resta, European Synch. Rad. Fac., France, J. Gustafson, N.M. Martin, Lund Univ., Sweden, A. Trincherro, P.-A. Carlsson, Chalmers Univ. of Tech., Sweden, O. Balmes, European Synch. Rad. Fac., France, J.N. Andersen, Lund Univ., Sweden, R. Feici, European Synch. Rad. Fac., France, E. Lundgren, Lund Univ., Sweden, H. Grönbeck, Chalmers Univ. of Tech., Sweden**

An important goal in surface science is to provide fundamental information on gas-surface interactions for the design of cheaper and more efficient catalysts. For this purpose, the required minimum knowledge is the composition of a catalyst for a certain reaction under realistic reaction conditions. Although this information seems trivial it is surprisingly difficult to obtain due to the complex structural nature of a real catalyst and the sometimes high temperatures and pressures under reaction conditions.

In the case of the complete oxidation of methane using Pd as the catalyst, pure Pd metal, Pd surface oxides and bulk PdO have all been reported to be most efficient to convert CH<sub>4</sub> into CO<sub>2</sub> and H<sub>2</sub>O [1-5]. This highlights the complexity of catalysis even for a relatively simple catalytic reaction.

In order to shed some light on the state of Pd during complete methane oxidation, we have performed in-situ Surface X-Ray Diffraction (SXRD) over a Pd(100) surface in a realistic reaction environment combined with DFT calculations. Our study demonstrates that significant roughening of the surface occur during the reaction, which increases the active surface area and thus affects the overall reactivity. Nevertheless, our study strongly suggests that the Pd metal is the most active phase for the full oxidation of methane.

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11:00am **IS+AS+SS-MoM9 The New Ambient Pressure X-ray Photoelectron Spectroscopy Instrument at MAX-lab - An Instrument also for Ultrahigh Vacuum Studies**, *J. Schnadt, J. Knudsen, A. Pietzsch, N. Johansson, A. Olsson, F. Hennies*, Lund University, Sweden, *N. Mårtensson, H. Siegbahn*, Uppsala University, Sweden, *J.N. Andersen*, Lund University, Sweden

Ambient pressure x-ray photoelectron spectroscopy (APXPS) is a technique, which dates back to the 1970s and 1980s, but which only during the past ten years has developed a very significant impact, driven forward especially by groups at the Advanced Light Source and BESSY. APXPS makes possible x-ray photoelectron spectroscopy (XPS) measurements under realistic or close-to realistic conditions, while conventional XPS is limited to vacuum conditions of 10<sup>-6</sup> mbar or better. APXPS thus contributes to closing the “pressure gap” of surface science, which has inhibited the understanding of processes and chemical reactions, for which the chemical potential of the gas atmosphere plays a decisive role. It also renders possible experiments on samples with a large vapour pressure, such as liquids or solid samples with a high degassing rate. Today, there exist a number of APXPS instruments around the world, including a small number of systems at synchrotrons. Common to these instruments is that they perform well at elevated pressures, but none of them is specifically designed to also allow studies under ultrahigh vacuum conditions. This complicates the connection to results from ultrahigh vacuum studies.

A new instrument for APXPS has just been installed at beamline I511 of the Swedish Synchrotron Radiation Facility MAX-lab. This instrument, which has been delivered by SPECS GmbH, Berlin, Germany, and which makes use of a PHOIBOS 150 NAP analyser, has been developed with the particular aim of building a strong link between ultrahigh vacuum and ambient pressure experiments and science. The instrument is capable of performing XPS measurements on the same sample in both types of environment. This is made possible by a unique design, which is based on the use of a retractable ambient pressure cell. For ambient pressure measurements at pressures of around 0.1 to 10 mbar the cell is docked to the electron energy analyser. Once the sample is loaded the cell is locked, and the only leak to the vacuum is through the nozzle of the analyser’s lens system. Hence, even during ambient pressure measurements the vacuum remains intact in the analysis chamber. For UHV measurements the cell together with the nozzle is retracted into a separate chamber, and UHV XPS measurements can be performed normally. This entails also another attractive feature of the instrument, namely, that the high pressure cell easily can be replaced by dedicated cells for other sample environments.

In this contribution the design and concept of the APXPS instrument at MAX-lab will be discussed and first results shown. Also plans for an upgraded and dedicated new beamline at MAX-lab will be presented.

11:20am **IS+AS+SS-MoM10 In Situ XPS and STM Studies of Ge<sub>2</sub>H<sub>6</sub> Interactions with the Si(100) Surface**, *S. McDonnell, J.F. Veyan*, University of Texas at Dallas, *J. Ballard, J.H.G. Owen, J.N. Randall*, Zyvex Labs, *Y.J. Chabal, R.M. Wallace*, University of Texas at Dallas

We present a study of the reactions between Ge<sub>2</sub>H<sub>6</sub> and Si(100) surfaces. Ge<sub>2</sub>H<sub>6</sub> is a potential precursor that could allow atomic layer epitaxy (ALE) on Ge(100) and Si(100) surface [1,2] which will be a vital component for atomically precise manufacturing (APM). We investigate the effects of various growth conditions such as substrate temperature, dosing pressure and post deposition annealing. We study the formation of seed layers for

ALE along with the reactions on both the atomically clean and the hydrogen passivated surfaces, where we see evidence of Ge<sub>2</sub>H<sub>6</sub> reacting with the dangling bonds.

To facilitate these studies, we utilize a UHV deposition/characterization tool. Chemical analysis of the surfaces is achieved using *in-situ* x-ray and ultraviolet photoelectron spectroscopy. Differences in the chemical states of germanium present on the surface under the various growth conditions are identified. This analysis is supplemented by *in-situ* scanning tunneling microscopy, which allows us to monitor the growth of germanium on silicon and confirm 2D or 3D growth. Comparisons are made with similar experiments carried out in a different UHV chamber where the surface is characterized with Fourier transform infrared spectroscopy (FTIR) and shows evidence of the digermane reacting with the surface at 173K as Ge<sub>2</sub>H<sub>5</sub> rather than GeH<sub>3</sub>.

This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

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# Monday Afternoon, October 31, 2011

Applied Surface Science Division

Room: 102 - Session AS-MoA

## Quantitative Surface Chemical Analysis and Technique Development - Part II

Moderator: M.S. Wagner, The Procter & Gamble Company

2:00pm **AS-MoA1 Surface-based Model Systems of Biomolecular Hydrogels - From Supramolecular Organization and Dynamics to Biological Function**, N.S. Baranova, S. Attili, CIC biomaGUNE, Spain, R.P. Richter, CIC biomaGUNE & MPI for Intelligent Systems, Spain

INVITED

Nature has evolved complex materials that are exquisitely designed to perform specific functions. Certain proteins and glycans self-organize *in vivo* into soft and dynamic, strongly hydrated gel-like matrices. Illustrative examples of such biomolecular hydrogels are cartilage and mucus. Although biomolecular hydrogels are ubiquitous in living organisms and fulfill fundamental biological tasks, we have today a very limited understanding of their internal organization, and how they function. The main reason is that this type of assemblies is difficult to study with conventional biochemical methods.

In order to interrogate biomolecular hydrogels directly on the supramolecular level, we have developed an unconventional approach that draws on knowledge from several scientific disciplines. Exploiting surface science tools, such as supported lipid bilayers, we tailor-make model systems by directed self-assembly of purified components on solid supports. With a toolbox of surface-sensitive analytical techniques, including quartz crystal microbalance, ellipsometry, atomic force microscopy and microinterferometry, these model systems can be investigated quantitatively and in great detail. From the experimental data, combined with polymer theory, we develop a better understanding of the relationship between the supramolecular organization and dynamics of biomolecular hydrogels, their physico-chemical properties and their biological function. To illustrate this concept, I will present some of our recent work on the "sweet" jelly-like matrix that forms around the mammalian egg during ovulation (the so-called cumulus cell-oocyte complex matrix) and that is crucial for fertility, and on the proteoglycan-meshwork that contributes to the load-bearing and lubricating properties cartilage.

2:40pm **AS-MoA3 Soft Cluster-Induced Desorption and Ionization of Biomolecules - Influence of Surface Load and Sample Morphology on Desorption Efficiency**, M. Baur, B.-J. Lee, HS Esslingen, Germany, C.R. Gebhardt, Bruker Daltonik, Germany, H. Schröder, K.-L. Kompa, MPI for Quantum Optics, Germany, M. Durr, HS Esslingen, Germany

Neutral cluster-induced desorption and ionization is a very soft method for transferring surface-adsorbed biomolecules into the gas phase [1]. Using neutral SO<sub>2</sub> clusters seeded in a He beam, the method makes use of the dipole moment of the cluster's constituents which allows both for solvation and charge transfer processes in the cluster [2]. Thus the cluster provides not only the energy for the desorption process but also serves as a transient matrix. As a consequence, desorption and ionization of oligopeptides and proteins is observed at low energies of the impacting clusters and without any fragmentation of the biomolecules.

Here we show that cluster-induced desorption and ionization of biomolecules can be efficiently applied for a wide range of surface concentrations and configurations, i.e. from  $\mu\text{m}$ -thick films down to surfaces prepared with submonolayer surface concentration of biomolecules. Highest signal intensity in the respective mass spectra was observed from thick films, indicating an efficient desorption mechanism from bulk-like material. In the submonolayer regime, the ion signal of the desorbed biomolecules was found to depend nonlinearly on surface concentration of the wet-chemically applied biomolecules. The behavior is traced back to the formation of multilayered islands of biomolecules on the surface, as observed by means of SEM and AFM, and a dominant contribution to the ion signal from these islands even at low coverage. With the current set-up and preparation scheme, the lower detection limit was shown to be  $10^{-13}$  mol.

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3:00pm **AS-MoA4 Sensitive Elemental Analysis of Materials via Femtosecond Ablation Time of Flight Mass Spectrometry**, J.F. Moore, MassThink, S. Milasinovic, Y. Cui, J.S. Penzak, Y. Liu, R.J. Gordon, L. Hanley, University of Illinois at Chicago

A new instrument is described which is capable of delivering  $\sim 70$  fs pulses of 800 nm light to a 100  $\mu\text{m}$  focus; this instrument can ablate small volumes (100-1000  $\mu\text{m}^3$ ) of material from a sample (e.g. a 10  $\mu\text{m}$  spot to a depth of 3  $\mu\text{m}$ ) and analyze the ions formed in the ablation process by time of flight and quadrupole mass spectrometry. Some novel features of this instrument include (1) a variable pressure source that allows collisional cooling of ions from the ablation plume, (2) the ability to use fs pulse pairs as well as temporally shaped laser pulses with a variable delay line to provide control over the ablation and ion formation process, and (3) a high velocity sample stage combined with a rapid data acquisition system that allows rapid scanning of materials at kHz repetition rate (of ablation events). Results from the ablation of elemental samples (Mg, Al, Si, Cu, Mo, Ag, Ta, Au) and metal alloys will be presented along with microscopy of ablation craters and a discussion of fluence dependence, useful yield, and instrumental sensitivity. Although the current system provides analysis on the micron scale, plans to extend its capability to the nanometer scale and to apply ablation to nanoparticles are being made and will be addressed.

3:40pm **AS-MoA6 Interlaboratory Study on Consistency and Reproducibility of Sputter Rate Measurements**, M.H. Engelhard, D.R. Baer, Pacific Northwest National Laboratory

The method and procedures used by many researchers doing sputter depth profiling has evolved from the experience of many researchers using several generations of sputter ion guns. Often considerable instrument time is used to establish the sputtering rate for specific instrument configuration and operating conditions at the time of analysis. We have conducted an inter-laboratory "round robin" study help identify the types of variations actually observed in sputtering systems in use today to help determine the time frame for which calibration may be needed, depending on the type of information required by the analysis. The depth of thin layers was identified as a major information need in surface analysis by surveys done for E42 and ISO TC201. This "round robin" was undertaken as an ASTM International Interlaboratory Study (ILS 229) The results obtained from this study will be used to determine a required frequency of ion gun sputter rate calibration and for the development of a guide or standard.

In this poster we present results obtained from seven ILS-229 participants. Each participant was sent a package containing 7 SiO<sub>2</sub> coupons with known thickness measured using a J. A. Woollam Co.  $\alpha$ -SE Spectroscopic Ellipsometer. The participants were asked to perform 5 depth profiles using identical ion gun settings at different time intervals: Immediately after turning the ion gun filament (minimal warm up), after a 60 minutes filament warm up period (typical warm up), at the end of the day (filament on all day), the following day (typical filament warm up of 60 min.), and after one week (typical filament warm up of 60 min.) The sputter rates were determined from a plot of the Si and O intensity as a function of sputter time. The time needed to sputter through the entire SiO<sub>2</sub> layer (when the O signal drops to 50% of the plateau value) is identified as the sputter time. The sputter time  $t_{sp}$  is determined using ASTM Standard Practice E 1636-04 "Analytically Describing Sputter-Profile and Linescan Profile data by an Extended Logistic Function". The results demonstrate both the excellent consistency of sputter conditions for many ion gun systems, but also the need to have a process to actually determine the stability of a specific ion gun system and configuration.

4:00pm **AS-MoA7 Post-Acquisition Mass Resolution Improvement in Time-Of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)**, S.J. Pachuta, P.R. Vlasak, 3M Company

Time-of-flight secondary ion mass spectrometers employing pulsed primary ion beams provide excellent mass resolution, on the order of 10,000 (full-width-at-half-maximum) over most of the spectral range. Unfortunately, even with all instrumental parameters optimized, ultimate mass resolution can only be achieved by sampling a relatively small area on a smooth surface oriented perpendicular to the extraction optics, under a uniform electric field. It is often difficult to meet these four criteria simultaneously.

These criteria fall into two categories, geometric and electrical. Mass resolution degradation due to geometric factors is the result of a distribution of flight times for ions of the same mass, caused by secondary ions originating from different vertical and horizontal positions within the analysis area, and, for rastered primary ion beams, by differences in the flight times of primary ions across the rastered area. Partial correction of these problems can be achieved in real time through hardware and software compensation, but the instrument must be well-tuned. For insulators,

electrical effects may be convoluted with geometric factors and influence mass resolution in a number of unpredictable ways.

For data acquired in “raw” mode (full spectrum at every pixel), it is sometimes possible to correct for these real-world difficulties after data acquisition. Two approaches are employed. The first involves subdividing the analysis area into a regular grid of smaller regions and extracting mass spectra from each region. The extracted spectra are individually calibrated by an automated process, and all or an optimized portion of the spectra are summed to produce a new spectrum with higher mass resolution than the original total spectrum. Interestingly, the spectral calibration information can be used as a diagnostic tool for instrument alignment and tuning.

The second approach is effective for improving mass resolution in spectra of rough surfaces, such as fabrics. Unlike the first approach, the analysis area is not subdivided into a regular pattern. Rather, spectra are obtained from regions of similar height, identified by any of four methods ranging from manual selection of regions-of-interest to automated pixel selection using principal component analysis and multivariate curve resolution. The automated methods have the advantage of simultaneously optimizing the mass resolution and the spectral counts without having to take a trial-and-error approach.

With these methods, mass resolution improvements of 20% - 50% are typical for smooth surfaces, and much larger improvements can be achieved for rough surfaces.

#### 4:20pm **AS-MoA8 ToF-SIMS Analysis of Iron Oxide Particle Oxidation by Isotopic and Multivariate Analysis.** *J. Ohlhausen, E. Coker, A. Ambrosini, J. Miller*, Sandia National Laboratories

A procedure for quantitative ToF-SIMS analysis of the re-oxidation of iron oxide particles in a ceramic matrix is discussed. Iron oxide is reacted with yttria stabilized zirconia (YSZ) to create a composite that facilitates the high temperature decomposition of CO<sub>2</sub> and H<sub>2</sub>O. In the two step process, Fe<sub>3</sub>O<sub>4</sub> is partially reduced to FeO by heating to high temperatures (>1300 °C) under inert atmosphere. It is then re-oxidized at < 1200 °C under CO<sub>2</sub> or H<sub>2</sub>O yielding CO or H<sub>2</sub> respectively. The reactivity of this two step solar-thermochemical process is being investigated by varying the concentration of iron in YSZ up to and past its solid solubility point, thus affecting the size of iron oxide particles in the matrix, and hence their rate and extent of re-oxidation. For the SIMS experiment, the YSZ sample containing natural abundance iron oxide was mixed with an organic binder, isostatically pressed into a disc and calcined in air at 1450 °C. This disc (~ 10mm diameter, 2mm thickness) was thermally reduced at 1400 °C and then re-oxidized at 1100 °C in the presence of C<sup>18</sup>O<sub>2</sub>. The ratio of <sup>18</sup>O to <sup>16</sup>O shows the extent of oxygen exchange for each iron oxide particle.

For ToF-SIMS analysis, samples are prepared by cross-sectioning and polishing by conventional metallographic preparation techniques followed by ion milling with Cs<sup>+</sup> in the ToF-SIMS. ToF-SIMS data are acquired from the cross section only after surface contaminants are removed and a “bulk” condition exists on the exposed surface. Data are acquired in a fashion that maximizes the ability to correct for detector saturation, thus providing quantitative oxygen isotopic results with little error. Data analysis method uses a combination of multivariate analysis for particle identification and conventional analysis for quantitative isotopic ratioing. Details of analysis procedures will be discussed along with results for a range of iron oxide particle sizes.

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

#### 4:40pm **AS-MoA9 Informatics for SIMS: Identifying Molecules in Complex Mass Spectra.** *I.S. Gilmore, F.M. Green, M.P. Seah, J.L.S. Lee*, National Physical Laboratory, UK

High-throughput screening using mass spectrometry for proteomics has driven the need to move from manual methods for protein identification to automated methods. Metabolomics has similar needs owing to the complex chemical mixtures studied. A combination of three important developments has allowed major progress in the automated interpretation of spectra to identify chemical and biological constituent substances. These are (i) the explosion in the amount of publicly available chemical information (PubChem<sup>1</sup>, for example indexes over 71 million substances) (ii) advances in mass spectrometry search engines and fragmentation tools and (iii) rapid growth in high performance mass spectrometers (mass accuracy < 1 ppm and mass resolution > 100,000). These recent developments in informatics are the endeavours of a very much larger community than the surface analysis community. We can utilise this rich resource.

We show this in three parts. Firstly, we analyze the popular PubChem database in terms of the population of substances with mass when resolved with typical mass spectrometer mass accuracies<sup>2</sup>. In general, in ToF-SIMS

the mass accuracy is ~ 30 ppm for an unknown substance. For a typical molecule (the modal mass in PubChem<sup>1</sup> is 385 u) there are ~ 30,000 substances within this mass tolerance<sup>2</sup>. In high performance mass spectrometers (~ 1 ppm mass accuracy) this range reduces to ~ 1000 substances which may be further reduced to around 50 substances using isotope pattern matching. Clearly, the mass accuracy in organic SIMS needs to improve significantly to benefit from chemical databases in the same manner as the metabolomics community. Secondly, we have previously shown how G-SIMS simplifies spectra so that the most structurally significant peaks are dominant and we now show a new development called the g-ogram<sup>3</sup>. This gives a visually simple chromatographic method to interpret spectra and allows separation of, for example, substrate, polymer and molecule peaks based on the fragmentation energy. Thirdly, we show how the G-SIMS spectra are a bridge to the informatics methods used by the metabolomics community providing identification automatically linked to public chemical databases. Present challenges and future opportunities will be discussed.

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#### 5:00pm **AS-MoA10 keV Ion Impact Effect on the IonCCD™ Surface and Mass Spectra Peak Shape in Non-Scanning Sector-Field Instrument.** *O. Hadjar, G. Kibelka, S. Kassan, C. Cameron, K. Kuhn, OI Analytical*

Particle-surface interactions are very important processes making physics practically impossible to apply without putting those interactions into the equation. For particle detection applications, the detection event is triggered by total or partial particle energy deposition upon impact on the detector. Mass spectrometry common ion detectors are Channeltrons and MCPs, which inherently destroy the particle upon measurement. The IonCCD, a product from the rapidly emerging technology will be characterized against keV ion impact when used in a dispersive mass analyzer.

The IonCCD is used as focal plane array in a sector field instrument of Mattauch-Herzog geometry (MH-MS). When miniaturized, MH-MS is best suited for low mass range applications (< 100 u). Differently from the two first detector families that most often operate in particle counting mode (time resolved detection) the IonCCD operates in an integration mode (charge integrator). In this case, dispersed ions neutralize on the electrode pixels for a well-defined time known as the integration time. While the potential energy of the detected ions is used for detection, the ion kinetic energy leads to ion-surface interaction, an artifact amplified at extreme low mass detection. This latter can be eliminated by floating the IonCCD or operating it in higher magnetic fields.

The artifact manifesting in the mass spectra as distortion (negative peak) due to keV ion impact induced secondary electron emission was modeled and investigated experimentally using electronic stopping power fingerprints. We demonstrate that the artifact increases linearly with ion impact velocity and is dependent in an oscillatory fashion on ion nuclear charge. Both findings are in agreement with the electronic stopping of keV ions with the TiN surface of the IonCCD. 3D simion modeling suggests efficient peak artifact suppression by operating the IonCCD in higher B-field (> 4000 G) and less elegantly by IonCCD-magnet face retarding field. Same model was used to enhance the performance of the instrument, confirming the dynamic mass range (Mmax/Mmin) increase from 16 to 70.

The potential IonCCD damage upon keV ion impact through the nuclear stopping effect was investigated by means of Atomic Force Microscopy and X-ray Photoelectron Spectroscopy. While AFM confirmed the expected increase in surface roughness, XPS showed no stoichiometry change due to implantation or preferential ion sputtering. The discoloration observed after extensive use was related to carbon layer formation in the roughened irradiated pixel area. Nuclear stopping effects do not seem to affect the detector performance at practical doses.

#### 5:20pm **AS-MoA11 First use of ToF-SIMS for Screening Assays: Enzymes Active on Wood.** *R.E. Goacher, E.A. Edwards, C.A. Mims, E.R. Master*, University of Toronto, Canada

Proteomic and metagenomic studies are rapidly increasing the number of proteins available for enzymatic screening. However, current high-throughput enzyme assays have limited applicability for an important class of biochemical substrates – complex solid materials. The present work aims

to utilize the strengths of Time-of-Flight Secondary Ion Mass Spectrometry for the direct measurement of enzyme activity on solid substrates. Particularly, ToF-SIMS is applied to the detection of wood-modifying enzymes.

Proof-of-principle ToF-SIMS enzyme assays were performed by immersing extracted wood fibers in solutions of commercial cellulase and laccase enzymes (utilizing water/buffer and denatured enzymes for controls). The laccase enzyme was also tested with and without several small molecule mediators. Principle Component Analysis (PCA) clearly distinguished cellulase tests from controls through the loss of polysaccharide peaks and relative enrichment of lignin peaks. Additionally, PCA distinguished laccase test samples (with mediator) from controls through a shift in lignin-characteristic peaks. The active laccase was indicated by a relative decrease in guaiacyl-lignin and syringyl-lignin peak intensities and increase in generic aromatic peaks, resulting from the cleavage of hydroxyl and methoxy groups from lignin benzoid units.

These proof-of-principle assays demonstrate that ToF-SIMS is capable of providing yes/no screening information for enzyme activity on complex solid substrates, such as wood.

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## In Situ Spectroscopy and Microscopy Focus Topic

Room: 106 - Session IS+AS+SS-MoA

### In Situ Characterization of Solids: Film Growth, Defects, and Interfaces

Moderator: M. Salmeron, Lawrence Berkeley National Laboratory

2:00pm **IS+AS+SS-MoA1 A New Approach to Defect Evolution Studies – Combined In Situ Experiments and Electron Tomography.** *I.M. Robertson, J. Kacher, G. Liu*, University of Illinois at Urbana-Champaign

INVITED

Electron micrographs are two-dimensional images capturing specific instances in the evolution of the microstructure and composition as well as the electronic and magnetic state. As these yields no insight as to how the state evolved, *a posteriori* knowledge is used to determine the most likely pathway. This challenge can be addressed by conducting experiments *in situ* in the transmission electron microscope, which allows direct observation and in some cases quantification of the reactions and interactions responsible for the evolved structure. The information, however, remains two-dimensional and with increasing use of this technique it is becoming apparent that lack of three-dimensional knowledge is hindering interpretation. Information in the beam direction can be recovered by applying electron tomography, but this is a relatively new technique to defect studies and despite its potential it remains a static snapshot. In this talk, I will illustrate how time-resolved deformation studies have improved our understanding of the behavior of dislocations and how this information has informed the development of new models. I will also demonstrate how three-dimensional images yield a better understanding of complex dislocation interactions and configurations. Finally, I will address the challenges faced in combining these two techniques such that three-dimensional snapshots of the evolving microstructure can be acquired periodically.

2:40pm **IS+AS+SS-MoA3 Real-time Oxide Growth Characterization using Atomic Force Microscopy.** *G. Rijnders*, University of Twente, the Netherlands

INVITED

Complex oxides have attracted great interest since they exhibit a rich spectrum of physical properties such as ferromagnetism, antiferromagnetism, colossal magnetoresistance, ferroelectricity, dielectricity, and superconductivity. Novel heteroepitaxial devices based on these complex oxides, like spin-polarized ferromagnetic tunnel junctions, superconducting devices and piezoelectric devices, have great potential and are currently under investigation in many groups.

The nature of the above-mentioned physical properties in complex oxides is determined by very small characteristic length scales, comparable to the unit cell lattice parameters of complex oxide. Because of these small characteristic length scales, growth control on an atomic level as well as understanding of the different mechanisms affecting the growth mode is essential for the fabrication of epitaxial heterostructures.

Two independent processes, i.e., nucleation and growth of islands, play an important role during vapor-phase epitaxial growth on an atomically flat surface. Here, nucleation causes the formation of surface steps and

subsequent growth causes the lateral movement of these steps. Both processes are determined by kinetics, since they take place far from thermodynamic equilibrium. These kinetic processes affect the final surface morphology and are, therefore, extensively studied. I will demonstrate the applicability of high-pressure RHEED as well as Scanning Force Microscopy (SFM) to monitor the growth of complex oxides during Pulsed Laser Deposition (PLD). Because of recent developments, SFM is nowadays also used to study dynamic processes, such as thin film growth and surface reaction mechanisms.

We have realized a system, in which SFM can be performed during Pulsed Laser Deposition (PLD). Deposition and force microscopy are performed in one vacuum chamber and via a fast transfer (in the order of seconds) the surface of a sample can be scanned. In our system we take advantage of the *pulsed* deposition process, because microscopy measurements can be carried out between the pulses. This provides real-time morphology information on the microscopic scale during growth. The transfer mechanism allows switching between microscopy and deposition with a reposition accuracy of  $\pm 500$  nm which gives new opportunities to study growth processes. Furthermore, it can provide information if RHEED is not possible, for example during amorphous and polycrystalline growth.

In this contribution, I will highlight recent advances in oxide thin film growth as well as the latest equipment developments.

3:40pm **IS+AS+SS-MoA6 An Auger Electron Analyzer System for In Situ MBE Growth Monitoring.** *W.L. Calley*, Georgia Institute of Technology, *P.G. Staib*, Staib Instruments, *J.E. Lowder, J.D. Greenlee, M.W. Moseley, W.E. Henderson, W.A. Doolittle*, Georgia Institute of Technology

Auger Electron Spectroscopy (AES) analysis is a surface sensitive technique for thin film analysis, able to detect nearly all elements [1]. Not only can AES help determine the species present at the surface, but AES can also yield information about the chemical bonding [1]. However, this analysis tool has historically been an *ex situ* technique with a few noted exceptions [2]. Herein we demonstrate the capabilities and usefulness of an Auger probe, the Staib *In situ* Auger Probe (SIAP) that has a sufficient working distance (tested up 82 mm) so as to not shadow beam fluxes allowing use during growth. The probe leverages an existing RHEED gun as an e-beam source for Auger electron excitation.

The configuration and operation of the SIAP has been described in detail [3]. The tool is installed on an MBE system configured for Terfenol growth, a miscible alloy of TbFe<sub>2</sub> and DyFe<sub>2</sub>. Initial growths performed without Auger monitoring exhibited substantial oxidation even after Ar etched to remove surface contamination, figure 1. The SIAP was then employed to determine the sources of oxygen contamination.

Three sources of O were identified. The growth chamber had a high enough partial pressure of oxygen to oxidize the highly reactive rare earth elements. After 30 hours in the chamber, uncapped Tb showed a substantial increase in the ratio of O to Tb, figure 2. The Tb source material also delivered O and the rate of O delivery increased with cell temperature, figure 3. A final oxygen source was identified to be the Tb/SiO<sub>2</sub> interface as shown in the SIMS data in figure 4. Figure 5 shows the Si wafer with C and O present at the surface. After growth is initiated the C is not detected after 40 Å of deposition, however, the O can be detected until 200 Å are deposited, indicating intermixing with the SiO<sub>2</sub> interface.

Further tests were conducted starting with a layer of Dy and depositing part of a monolayer of Tb in 2% increments. Figure 6 shows a clear distinction between bare Dy and 2, 4, 6, 8, and 10% monolayer coverage of Tb on a Dy layer, demonstrating the SIAP's sensitivity is at least 2% of a monolayer for these heavy elements.

The SIAP is complementary to existing RHEED systems. While RHEED gives information about the crystal structure of the growing film, the SIAP provides chemical information. This is especially useful when working with films without line compositions. The SIAP coupled with a future closed loop control system may enhance growth of films with multiple oxidation states or other similar phase/chemical transitions. Finally this technique could give information about transitions between layers in multilayered films grown via MBE.

4:00pm **IS+AS+SS-MoA7 Quantum Size Effect Driven Structure Modifications of Bi-films on Ni(111).** *T.R.J. Bollmann, R. van Gastel, H. Zandvliet, B. Poelsema*, University of Twente, The Netherlands

We have investigated the initial growth of Bi/Ni(111) using Low Energy Electron Microscopy (LEEM) and Selected Area Low Energy Electron Diffraction ( $\mu$ LEED). Bismuth represents an interesting material since 1) it has a tendency for allotropism, 2) it forms several ordered alloys with Ni and 3) with Bi being a neighbor of Pb in the periodic system, one may find evidence for quantum size effects in ultrathin Bi layers. Indeed we obtain



ample evidence for Bi/Ni(111) as being a very rich system, even at a fixed substrate temperature of 474 K.

We find first that the deposition of Bi leads to the formation of a surface alloy with a  $(\sqrt{3}\times\sqrt{3})\text{-R}30^\circ$  structure at a Bi-coverage of 1/3. Continued Bi deposition leads to the formation of an incommensurate wetting layer with a continuously decreasing lattice parameter, finally ending in a  $(7\times 7)$  structure. From the variation of the step position at the buried interface, nicely accessible with LEEM, we conclude that the dealloying of the  $\sqrt{3}$  phase is incomplete and that the  $(7\times 7)$  wetting layer in fact involves two layers with a small, but finite Bi content in the second layer. Upon further Bi deposition elongated, 3-4 layers high nanowires emerge, with a  $p(5\times 2)$  structure and a width of about 80 nm, oriented along  $\langle 110 \rangle$  and  $\langle 100 \rangle$ -azimuths. Further deposition of Bi-leads to different (sometimes coexisting) structures:  $(3\times 3)$ -patches with a thickness of three atomic layers and patches with a matrix structure ( $m_{11}=3$ ,  $m_{12}=-1$ ,  $m_{21}=1$ ,  $m_{22}=2$ ) and a thickness of five atomic layers. This accurate height assignment is uniquely enabled by the analysis of LEEM-IV data.

The results are fully consistent with quantum size effect driven thin film morphology: the different film structures and their thicknesses nicely fit with integer numbers of nodes in their specific Fermi wave function, even for the seven layers thick  $(7\times 7)$  structure obtained at a lower temperature of 422 K. Tensor LEED calculations of the interlayer spacing of the different structures concur with this assignment.

The influence of the structure and morphology on electronic properties of various materials is well known. The interaction between electronic and crystal structure should be reciprocal. The Bi/Ni(111) system provides a nice and we think first illustration: electronic properties, in particular quantum size effects, actually drive the structure of the thin bismuth films.

4:20pm **IS+AS+SS-MoA8 Growth and Structure of Sm on an Ultrathin  $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$  Film: A Comprehensive Study, J.F. Zhu, Q. Xu, S. Hu, X. Feng, D. Chen, University of Science and Technology of China**

The growth and electronic structure of vapor-deposited Sm onto a well-ordered  $\text{Al}_2\text{O}_3/\text{Ni}_3\text{Al}(111)$  ultrathin film under ultrahigh vacuum (UHV) conditions at room-temperature has been studied comprehensively using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), scanning tunneling microscopy (STM) and low electron energy diffraction (LEED). Our results indicate that at room temperature Sm grows in a layer-by-layer fashion for the first two layers, followed by three-dimensional (3D) growth. The interaction of Sm with  $\text{Al}_2\text{O}_3$  thin films is so strong that deposited Sm is immediately oxidized at beginning. Both the oxidation states of  $\text{Sm}^{2+}$  and  $\text{Sm}^{3+}$  are found at low coverages ( $<1$  ML) with the situation that the concentration of  $\text{Sm}^{2+}$  dominates below 0.2 ML and subsequently that of  $\text{Sm}^{3+}$  dominates. With increasing Sm coverage, the metallic state of Sm gradually appears. Annealing the film of 0.2 ML  $\text{Sm}/\text{Al}_2\text{O}_3$  at  $T < 500$  K results in further oxidation of the Sm species where all the  $\text{Sm}^{2+}$  species converts to  $\text{Sm}^{3+}$ . Further annealing at higher temperatures leads to loss of Sm from the surface via subsurface diffusion.

4:40pm **IS+AS+SS-MoA9 In Situ Study of the Reaction Mechanism Kinetics of Pt ALD from  $(^{106}\text{Cp})\text{PtMe}_3$  and  $\text{O}_2$ , I.J.M. Erkens, A.J.M. Mackus, H.C.M. Knoops, F. Roozeboom, W.M.M. Kessels, Eindhoven University of Technology, Netherlands**

Atomic layer deposition (ALD) of noble metals and noble metal oxides on high-aspect-ratio 3D nanostructures has a wide variety of potential applications in sensing and catalysis. Despite several studies,<sup>1-3</sup> much is still unknown about the reaction mechanism of Pt ALD using  $(^{106}\text{Cp})\text{PtMe}_3$  and  $\text{O}_2$ , which can be considered a model system for noble metal ALD processes. Questions remain regarding the surface species and reactions, and the temperature dependence of the growth per cycle (GPC). In this contribution we expand the understanding of the Pt ALD mechanism by combining quadrupole mass spectrometry (QMS) and spectroscopic ellipsometry (SE). Using these in-situ techniques to study the process as a function of temperature between 100 and 300°C, we have gained a unique perspective, which has led to several new insights. The time-resolved QMS data for  $\text{CH}_4$  and  $\text{CO}_2$  show that combustion and other ligand reactions at the surface occur in sequence, while competing for the available carbon atoms. Quantification of the data showed that approximately 80% of the C atoms are combusted during the  $\text{O}_2$  pulse. By performing the QMS measurements in a temperature series, valuable information was obtained on the rate of combustion of the hydrocarbon ligands at the Pt surface during the  $\text{O}_2$  pulse. Using a combination of QMS and SE data, we were able to formulate a mechanism explaining growth inhibition at low temperatures. This mechanism manifests itself through three temperature dependent growth regimes: no growth below 100°C; limited growth between 100 and 250°C; and full growth between 250 and 300°C. Using results from surface science literature a likely explanation for these regimes

was given. This involves the cyclopentadienyl ligands at the Pt surface forming reactive intermediates or being thermally decomposed. The mechanism was corroborated by QMS and SE data on post-plasma treatment cycles, by which catalytic activity was temporarily restored. We were therefore able to link the temperature dependence of the GPC to combustion kinetics. A detailed description of our methods and results will be given in our contribution.

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2. Kessels *et al.*, *Appl. Phys. Lett.* **95**, 013114 (2009).

3. Setthapun *et al.*, *J. Phys. Chem. C* **114**, 9758 (2010).

5:00pm **IS+AS+SS-MoA10 In Situ Surface Analytical Characterization of Electronic Devices: Thin Film Solar Cells and Lithium Ion Batteries as Examples, A. Thissen, SPECS Surface Nano Analysis GmbH, Germany**

Electronic devices have revolutionized everyday life in industrial countries over the last decades. Especially devices for energy conversion and storage like thin film solar cells and lithium ion batteries are of importance for the future. Recently two main tasks for research and development are dominant: miniaturization for sophisticated applications targeting at the nanoscale, and designing low cost large scale devices. In both fields the device performance is strongly determined by materials quality, composition, combination and last but not least by processes at materials interfaces. Nanostructures, minimization of material consumption and the need to improve device efficiencies consequently leads to the widespread focussing on thin film preparation. For thin film devices surface and interface analysis like photoelectron spectroscopy and surface (spectro-)microscopies are an important tools for material and device characterization. Classical well defined model experiments already reveal important insights using highly integrated vacuum systems for analysis and preparation. But analysis of materials and devices under near ambient conditions and even in situ during operation is an inevitable future development to improve the significance of data for development and quality management. In this respect the application of techniques like Near Ambient Pressure XPS, XPS from liquids and solid liquid interfaces, hard x-ray PES (HAXPS), Near Ambient Pressure SPM on solar cell and lithium ion battery materials is the challenging tasks for manufacturing companies of surface analytical equipment.

# Tuesday Morning, November 1, 2011

## Applied Surface Science Division

Room: 102 - Session AS-TuM

### Imaging and 3D Chemical Analysis

Moderator: V.S. Smentkowski, GE-GRC, X. Dong, Eli Lilly and Company

8:00am **AS-TuM1 Recent Applications of GCIB Depth Profiling with XPS and TOF-SIMS**, T. Miyayama, N. Sanada, ULVAC-PHI Inc., Japan, J.S. Hammond, Physical Electronics **INVITED**

The development of new electronic devices incorporating organic materials, such as Organic Light Emitting Diodes (OLED's) and Organic Photovoltaics (OPV's) is rapidly increasing. To control quality, performance and lifetimes of these devices, it is necessary to characterize the layer structures and the dopant distributions in the thin organic materials. Conventional surface analysis techniques such as XPS and TOF-SIMS, combined with mono-atomic ion beam sputtering, have been widely used for chemical depth profiling of inorganic thin films. However, this approach has not been successful for the depth profiling of organic materials due to the loss of chemical information during the sputtering process. Recent cluster ion beam developments utilizing C<sub>60</sub> and Coronene ions have also had limited success for the XPS and TOF-SIMS depth profiling of OLED and OPV structures due to similar modification of chemical and molecular information as a function of sputter depth.

The chemical depth profiling of organic layers with thicknesses greater than one micron has also been problematic utilizing XPS and TOF-SIMS with C<sub>60</sub> cluster sources. The implementation of new cluster ion sources that could extend chemical depth profiling of organics to more than several microns should also expand the applications of the XPS and TOF-SIMS techniques.

Recent studies have shown the successful use of a GCIB (gas cluster ion beam) source on XPS (X-ray photoelectron spectroscopy) instruments to quantify the chemical depth profile of polyimide films without sputter induced chemical degradation<sup>[1, 2]</sup>. Based on these earlier experiments, additional GCIB depth profiling applications of organic and biomaterials with XPS and TOF-SIMS will be discussed. Examples will be presented for the characterization of ultra-thin organic electronic layers in OLED's and OPV's. The successful organic depth profiling to depths of several tens of microns will also be discussed.

1. Takuya Miyayama, Noriaki Sanada, Mineharu Suzuki, John S. Hammond, S.-Q. D. Si and Atsushi Takahara, *J. Vac. Sci. Technol. A* **2010**, A 28(2), L1

2. Takuya Miyayama, Noriaki Sanada, Scott R. Bryan, John S. Hammond and Mineharu Suzuki, *Surf. Interface Anal.* **2010**, 42, 1453-1457.

9:00am **AS-TuM4 Advances in Organic Depth Profiling for Polymer Devices**, J.L.S. Lee, I.S. Gilmore, National Physical Laboratory, UK, A. Licciardello, University of Catania, Italy

Knowledge of the distribution of organics within an organic matrix is important to the innovation and manufacture of many advanced technologies including polymer electronics and photovoltaics, medical devices, ink-jet printing technologies and drug delivery systems. Organic depth profiling using sputtering with cluster ions and imaging by SIMS or XPS have revolutionised the analytical capability for these important systems, providing uniquely detailed 3D chemical information. However, despite recent progress, organic depth profiling is not yet routinely applied to industry problems. The principal reason for this is that organic sputtering only works for a limited set of materials [1] and unfortunately it fails completely for many industrially important materials, such as conjugated polymers in the organics electronics industry. Consequently, an important recent development is the use of nitric oxide (NO) flooding [2] as a radical scavenger to reduce ion induced cross-linking during depth profiling.

In this study, we use model polymer layers, including polystyrene and industrially relevant conjugated polymers, to demonstrate the benefits of using NO flooding for polymers that do not sputter under normal conditions and evaluate the basic metrology. Understanding the mechanisms for damage, cross-linking, radical generation and radical reaction is vital in developing this technique to work with industrial materials. Using C<sub>60</sub><sup>2+</sup> as a sputtering ion beam, it is found that NO flooding combined with sample cooling [3] significantly reduce the disappearance cross-section for characteristic fragments. For polystyrene model systems, the steady state intensity of C<sub>7</sub>H<sub>7</sub><sup>+</sup> can be increased from typically < 0.1% of the initial intensity at normal experimental conditions to 50% when NO flooding is used in conjunction with cooling. We also demonstrate successful depth

profiles on 1 μm thick polymer material, showing high and constant sputtering yields with ~ 30 nm depth resolution to the interface. Our results show a dramatic improvement for the depth profiling of difficult type II polymers. NO flooding may be used along with other developments e.g. large argon cluster ions [4], sample cooling and sample rotation [3], and has the potential to provide a step change in analytical capability for industrial samples.

[1] C. M. Mahoney, *Mass Spectrom. Rev.*, **2010**, 29, 247

[2] N. Tuccitto, I. Delfanti, V. Spampinato and A. Licciardello, presented at SIMS XVII, Toronto, **2009**.

[3] P. Sjøvall, D. Rading, S. Ray, L. Yang and A. G. Shard, *J. Phys. Chem. B*, **2010**, 114, 769.

[4] J. L. S. Lee, S. Ninomiya, J. Matsuo, I. S. Gilmore, M. P. Seah and A. G. Shard, *Anal. Chem.* **2010**, 82, 98.

9:20am **AS-TuM5 TOF-SIMS Depth Profiling and 3D Analysis of Polymer Materials Using C<sub>60</sub> and Ar Cluster Ion Beams for Sputtering**, D. Rading, ION-TOF GmbH, Germany, N. Havercroft, ION-TOF USA, Inc., R. Moellers, E. Niehuis, ION-TOF GmbH, Germany

Preservation of molecular information under high-dose sputtering conditions has become increasingly important. It is not only a pre-requisite for depth profiling and 3D analysis of organic materials, but also extends the survival of sample material beyond the static SIMS limit in high lateral resolution imaging. In this respect, the use of a high energy cluster ion beam for sputtering such as SF<sub>5</sub> [1] and C<sub>60</sub> [2-4] has aroused considerable interest. With the beam energies typically applied, the total energy is high enough for reasonable sputter rates whereas the energy per atom, of about several 100 eV, is considered low enough to minimize sample damage. However, it has been demonstrated that a variety of organic compounds cannot be profiled in a satisfactory way and characteristic molecular secondary ion signals are lost [5-7]. In this respect it has been shown recently that massive argon cluster ions can be successfully applied as primary projectiles in SIMS [8,9].

We equipped a TOF-SIMS 5 instrument with a Bi<sub>n</sub>, C<sub>60</sub> and an Ar<sub>n</sub> cluster ion source in order to compare the possibilities and limitations of these projectiles for depth profiling of polymer materials. In this contribution, we will focus on dual beam depth profiling where the analysis is done with Bi<sub>n</sub> and the sputtering with C<sub>60</sub> and Ar<sub>n</sub> cluster ion beams, respectively. Stability and intensity of characteristic high mass molecular ion signals as well as sputter yields and depth resolution will be compared. For this purpose different beam energies resulting in 2 - 10 eV/atom for Ar<sub>n</sub> and 167 - 667 eV/atom for C<sub>60</sub> sputtering have been applied to various polymer samples. From our experiments we can conclude that most of the limitations C<sub>60</sub> sputtering suffers from could be successfully overcome and that the Ar GCIB seems to be a more universal tool for sputtering of organic materials.

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[3] J. Cheng, A. Wucher and N. Winograd, *J. Phys. Chem. B*, **2006**, 110, 8329-8336

[4] J.S. Fletcher, X.A. Conlan, J.C. Vickerman, N.P. Lockyer, *Appl. Surf. Sci.* **2006**, 252, 6513-6516

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[6] R. Möllers, N. Tuccitto, V. Torrisi, E. Niehuis, A. Licciardello, *Appl. Surf. Sci.* **2006**, 252, 6509-6512

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[8] N. Toyoda, J. Matsuo, T. Aoki, I. Yamada, D.B. Fenner, *Nucl. Instr. and Meth. in Phys. Res.* **2002**, B 190, 860-864

[9] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, *Rapid Communications in Mass Spectrometry* **2009**, 23, 1601-1606

9:40am **AS-TuM6 The zcorrectorgui for 3D ToF-SIMS Depth Profiles**, D.J. Graham, M. Robinson, D.G. Castner, University of Washington

ToF-SIMS imaging is a powerful technique for obtaining chemically specific maps of the surface of a wide range of samples including polymers, metals, tissues, and cells. When combined with the sputtering capabilities of modern ToF-SIMS instruments, one can obtain chemically and biologically specific 3D depth profiles, as well as track chemical signatures throughout a sample volume. This is done with a dual beam approach by taking an image of the surface, sputtering away a given amount of the material and then taking a new image of the freshly exposed area. This process is repeated until the object of interest is gone or the desired depth is reached.

When working with surfaces with significant topography such as the surface of a cell, the z axis of the resulting data cube is not correct. This is

due to the fact that each image slice of the surface is displayed as a 2-D image taken from a 3-D surface. This results in a type of inverted topography of the 3D structure within the ToF-SIMS image volume. To correct for this, the National ESCA and Surface Analysis Center for Biomedical Problems NESAC/BIO (Seattle, WA) has developed a Matlab (Mathworks, Natick MA) toolbox to correct the z-axis of cell depth profiles and display the data properly.

Since the shape and topography of a cell can be complex, we have created a set of features of known chemistry and controlled geometry in order to test and validate that the zcorrectorgui is accurately correcting the z-axis. For this, microsphere templating was combined with capillary force lithography to create features of known size and shape. The features sizes were chosen to correspond with the sizes of typical eukaryotic cells. Topographical images of these features were obtained by AFM. After AFM analysis the features were depth profiled by ToF-SIMS. The resulting depth profile data was then imported into the zcorrectorgui and processed. In this presentation we will highlight the results from this study and show example data obtained from a real cell depth profile processed with the zcorrectorgui.

10:40am **AS-TuM9 3D Analysis of Organic Multilayer Structures by TOF-SIMS Using Ar Cluster Ions**, *R. Moellers*, ION-TOF GmbH, Germany, *R. Kersting*, TASCION GmbH, Germany, *D. Rading*, *E. Niehuis*, ION-TOF GmbH, Germany

Organic multilayer systems are of increasing importance in many technological fields. The entry of the OLED technology into commercially available multi-color displays is one example. Optimization of this technology in terms of lifetime and efficiency requires a detailed knowledge of the layer and interface composition.

From the analytical point of view, these OLED multilayer structures are quite challenging. A detailed analysis requires the identification of complex high mass organic molecules in thin layers of only several nanometer thickness with a lateral resolution in the micrometer range. In particular the identification of the molecular composition is challenging for SIMS as molecular information does usually not survive high dose sputtering conditions.

In the past different projectiles such as low energy Cs<sup>+</sup> [1] and keV C<sub>60</sub><sup>+</sup> cluster [2-4] have been explored for their depth profiling capabilities on organic layers. For some materials molecular information survives but for the majority of organic molecules depth profiling using these projectiles fails. Recently the application of large Ar clusters for the non-destructive removal of organic matter has been discussed in the SIMS community. The GCIB (gas cluster ion beam) technique was developed by the group of Isao Yamada [5] at the University of Kyoto and has already demonstrated some potential in this field of application [6].

We used a TOF-SIMS 5 instrument equipped with a Bi cluster ion gun for the analysis and an Ar GCIB as well as an C<sub>60</sub> cluster ion gun providing both analysis and sputter gun capabilities. In this contribution we will focus on the variation of the sputter projectile, the energy dependence of the resulting depth resolution and the survival of specific molecular ion signal under high dose sputtering conditions. For this purpose a well-defined multilayer model sample similar to a working OLED device was used. The knowledge about the optimum analysis conditions gained on the model system was transferred to a 3D analysis of an OLED display device using an Ar GCIB for sputtering.

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[5] I. Yamada, J. Matsuo, N. Toyoda, A. Kirkpatrick; *Materials Science and Engineering: R-Reports. A Review Journal*; **34**, **2001**, 6, 231-295

[6] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, *Rapid Communications in Mass Spectrometry* **2009**, 23, 1601-1606

11:00am **AS-TuM10 Molecular Imaging of Cells and Tissues with Novel Ion Beams**, *J. Matsuo*, QSEC, Kyoto University, CREST, Japan, *K. Ichiki*, *T. Yamamoto*, *Y. Yamamoto*, Kyoto University, Japan, *S. Ibuki*, QSEC, Kyoto University, CREST, Japan, *T. Aoki*, *T. Seki*, Kyoto University, CREST, Japan

The field of secondary ion mass spectrometry (SIMS) for biological material analysis is receiving much attention nowadays, because molecular, structural and chemical information is considered to be invaluable. However, for large biomolecules the sensitivity of SIMS needs to be improved. Cluster ion beams have been reported to enhance the yields of secondary ions, because of the high-density energy deposition and multiple

collisions near surfaces. SF<sub>5</sub>, C<sub>60</sub>, Au<sub>3</sub> and Bi<sub>3</sub> were found to be quite useful for SIMS of organic materials.

We have proposed using a large Ar cluster beam for organic SIMS. This beam has a number of advantages over other cluster beams for molecular depth profiling of various polymers, and it provides new opportunities for sputtering molecules without inducing significant damage [1]. Biomolecules are also very fragile and thus difficult to sputter with conventional ion beams; therefore, a large Ar cluster beam would be quite suitable for biological material analysis. However, molecular imaging requires a focused Ar cluster beam, and we developed a new Ar cluster ion gun aiming to obtain a fine-focused beam of several mm diameter. An orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer, which allows the use of a continuous beam, was also combined in the system, and a mass resolution higher than 6000 was obtained. Because there was no need to use the ion-bunching technique in this system, there was no tradeoff between beam diameter and mass resolution. This is another advantage of this molecular imaging system over the conventional TOF instrument. This novel system is quite useful for both molecular depth profiling and imaging.

The latest results of this system and its performance in molecular imaging of cells and tissues will be presented and discussed.

[1] J. Matsuo, S. Ninomiya, H. Yamada, K. Ichiki, Y. Wakamatsu, M. Hada, T. Seki and T. Aoki, *Surf. Interface Anal.* (2011) 42, 1612

11:20am **AS-TuM11 High Resolution TOF-SIMS Imaging of Barrier Layers in Mouse Skin Stratum Corneum**, *I. Ishizaki*, ULVAC-PHI inc., Japan, *A. Kubo*, Keio University, Japan, *Y. Ohashi*, *A. Yamamoto*, ULVAC Inc., Japan, *J.S. Hammond*, *G.L. Fisher*, *S.R. Bryan*, Physical Electronics

The stratum corneum (SC) is the outermost layer of epidermis that acts as a barrier to keep foreign objects out of the body and to keep water in. It is composed of multi-layered sheets of dead cells containing keratin that continuously fall off and are regenerated from live cells in the underlying layers. The total thickness of the SC layer is less than 40 μm. In order to study the barrier properties of the SC and how this function fails in certain skin disorders, it is necessary to visualize the distribution of different biomolecules within the multi-layered SC structure. It is also valuable to compare the penetration of various foreign chemicals into the SC layer in mice with and without the skin disorder. In this initial study, we applied TOF-SIMS imaging using a bismuth cluster ion beam to characterize the multi-layer structure of mouse skin. Samples were prepared by quick freezing of mouse tails followed by cross-sectioning by cryostat. TOF-SIMS imaging provided the spatial resolution and molecular specificity to clearly visualize dead cell layers and living layers of the epidermis. By using peaks characteristic of specific molecules, it was possible to image the distribution of amino acids, cholesterol, and lipids within the SC. The results suggest that SC might contain several chemically distinct layers. Skin samples were also depth profiled using GCIB sputtering. Imaging of cross-sections and depth profiling from the skin surface will be compared for obtaining molecular profiles within the SC structure.

## **In Situ Spectroscopy and Microscopy Focus Topic Room: 106 - Session IS+AS+SS-TuM**

### **In Situ Studies of Organic and Soft Materials and Liquid-Solid Interfaces**

**Moderator:** A.I. Frenkel, Yeshiva University

8:00am **IS+AS+SS-TuM1 Solid-Vacuum, Solid-Gas, and Solid-Liquid Interfaces: Structure and Dynamics under Environmentally Relevant Conditions**, *M. Salmeron*, *C. Escudero*, Lawrence Berkeley National Laboratory **INVITED**

Surfaces play a fundamental role in many of today's frontier topics, such as clean and renewable energies, efficient and highly selective chemical processes (green catalysis), high capacity rechargeable batteries and fuel cells, and also environmental problems. To advance our For this it is imperative to develop new fundamental approaches to the study of the interface of solid materials with gases, liquids and solids, because it is in these environments that crucial processes occur that need to be understood to enable game-changing discoveries.

One way to control the structure of interfaces and their properties is through the design of materials of nanoscale dimensions, with specific shape, size and composition. It is equally imperative to develop and use techniques for in situ atomic level structural and spectroscopic characterization of the interfaces. New advances in instrumentation are fulfilling this need. I will illustrate this with examples from research carried out in my laboratory, which include scanning tunneling microscopy (STM), photoelectron and x-ray absorption spectroscopies (PES) under ambient conditions, for studies

of catalyst models, thin films, single crystals and nanoparticles, for applications in catalysis and electrochemistry. The results obtained so far demonstrate that the information obtained with these new techniques is unique and could not have been obtained or extrapolated from other more traditional surface sensitive techniques.

**8:40am IS+AS+SS-TuM3 Imaging Tagged Proteins in Whole Eukaryotic Cells in Liquid with Scanning Transmission Electron Microscopy, N. De Jonge, D.B. Peckys, Vanderbilt University School of Medicine INVITED**

We have recently introduced a novel electron microscopy technique for the imaging of whole cells in aqueous media using scanning transmission electron microscopy (STEM) [1, 2]. Eukaryotic cells in liquid were placed in a microfluidic chamber with a thickness of 5 - 10  $\mu\text{m}$  contained between two ultra-thin electron-transparent windows. On account of the atomic number (Z) contrast of the STEM, nanoparticles of a high-Z material (e.g., gold) were detected within the background signal produced by a micrometers-thick layer of a low-Z liquid (e.g. water, or cellular material). Nanoparticles specifically attached to proteins can be used to study protein distributions in whole cells in liquid, similar as proteins tagged with fluorescent labels can be used to study protein distributions in cells with fluorescence microscopy.

COS7 fibroblast cells were labeled with gold nanoparticles conjugated with epidermal growth factor (EGF). Intact fixed cells in liquid were imaged with STEM with a spatial resolution of 4 nm and a pixel dwell time of 20 microseconds [1]. In test experiments we demonstrated a maximal spatial resolution of 1.5 nm on gold nanoparticles placed above a water layer of a thickness of 3 micrometer, consistent with theoretical predictions, and with Monte Carlo simulations of the STEM imaging [3]. The use of quantum dots (QDs), which are fluorescent nanoparticles, allowed STEM images to be correlated with fluorescence images [4]. Eukaryotic cells were grown directly on microchips for the microfluidic chamber, fixed, and imaged with fluorescence microscopy. The intact cells were then imaged in liquid with STEM. The STEM images showed individual QDs, and their locations were correlated with the cellular regions, as imaged with fluorescence microscopy. We have also demonstrated the imaging of nanoparticle uptake in live cells [5], and the ultrastructure of pristine yeast cells was studied [6]. Liquid STEM presents an innovative approach for the imaging of whole cells, with significantly improved spatial resolution and imaging speed over existing methods.

URL: <http://www.mc.vanderbilt.edu/labs/dejongelab/>

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- [5] Peckys, D.B. & N. de Jonge, Nano Lett. 11, 1733-1738, 2011.
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**9:20am IS+AS+SS-TuM5 Imaging Live Cells in Liquid with Scanning Transmission Electron Microscopy, D.B. Peckys, N. De Jonge, Vanderbilt University School of Medicine**

We have applied a novel electron microscopy technique, referred to as liquid scanning transmission electron microscopy (liquid STEM) [1, 2] for the imaging of live eukaryotic cells. In two separate experiments, we studied a) nano particle (NP) uptake in COS-7 cells [3], a green monkey kidney fibroblast cell line, and, b) the ultrastructure of *Schizosaccharomyces pombe* cells [4], also known as fission yeast. The cells were confirmed to be alive at the onset of the liquid STEM imaging using specific fluorescent, live indicating dyes and correlative fluorescence microscopy. For the STEM imaging in liquid the cells were placed (in liquid) in a microfluidic chamber. The chamber had two ultra-thin electron-transparent windows allowing the passage of electrons and photons. The dimensions of the COS-7 cells required a thicker liquid filled space in the microfluidic chamber compared to the experiments with the fission yeast cells, and contrast was mainly obtained on the gold NP's. However, the thinner *S. pombe* cells allowed a thinner liquid layer, and images were recorded of the cellular ultrastructure.

Despite the fact, that the cells were not anymore alive after the STEM imaging, we consider the first STEM images taken from a cell or a specific cellular region, to represent the unperturbed and therefore physiological state. We derived this assumption after evaluation of the STEM images for

signs of radiation damage at the achieved resolution. Our STEM results were found to be consistent with known data about intracellular NP trafficking and storage in mammalian cells and data about the dimensions and distribution of organelles in fission yeast.

In conclusion, we have demonstrated the feasibility of STEM imaging live eukaryotic cells. The advantages of this approach are a) a several-fold higher resolution than live cell imaging with conventional light microscopy, b) a much faster (hours versus days) sample preparation than needed for conventional transmission electron microscopy (TEM) imaging of cells, c) absence of artifact introduction associated with conventional TEM sample preparation, and d) no need for introducing any kind of labels in order to achieve a similar range of resolution as possible with the new nanoscopic imaging techniques.

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**9:40am IS+AS+SS-TuM6 Microscopic Imaging of Biological Samples using Coherent Soft X-rays from Free-Electron Laser and Synchrotron Sources, T. Gorniak, T. Senkbeil, M. Beckers, C. Christophis, University of Heidelberg, Germany, K. Giewekemeyer, University of Göttingen, Germany, M. Grunze, University of Heidelberg, Germany, T. Salditt, University of Göttingen, Germany, A. Rosenhahn, University of Heidelberg, Germany**

Coherent X-ray microscopy of hydrated biological samples – especially in the so-called water window of 284-540 eV – is of tremendous interest for life sciences due to the high contrast of organic matter with respect to the aqueous background. Especially free-electron lasers can provide highly intense and coherent pulses, which allow single pulse imaging to overcome resolution limits set by radiation damage. We present the first holographic microscopy images of dehydrated biological material acquired in the water window with higher harmonic radiation provided by the free-electron laser FLASH. In order to increase the photon flux we used high efficiency zone plates instead of pinholes to create the divergent light cone for holography. The results pave the way to the vision of holographic imaging of hydrated biological samples with single FEL pulses. We supplement single pulse imaging experiments byptychographic imaging with synchrotron radiation at BESSY II. This method uses coherent diffraction imaging at different sample positions while maintaining a fixed spatial overlap between the fields of view. By introducing this spatial redundancy to the data an additional constraint for the iterative reconstruction algorithm is achieved. This enhances the convergence of phase retrieval drastically. The spatial resolution of below 50 nm and the imaging properties were characterized using lithographic and biological test samples. We also show results on resonant imaging with chemical contrast caused by both, absorption and phase shifts, in the vicinity of core level absorption edges.

**10:40am IS+AS+SS-TuM9 Surface Chemistry of Amino Acids at Near Ambient Pressure of Water Vapor, A. Shavorskiy, Lawrence Berkeley National Laboratory, T. Eralp, The University of Reading, UK, F. Aksoy, Nigde University, Turkey, M.E. Grass, Z. Liu, H. Bluhm, Lawrence Berkeley National Laboratory, G. Held, The University of Reading, UK**

The co-adsorption of water with organic molecules under near-ambient pressure and temperature conditions opens up new reaction pathways on model catalyst surfaces that are not accessible in conventional ultra-high vacuum surface-science experiments. The surface chemistry of glycine and alanine at the water-exposed Cu{110} and Pt{111} interface was studied both in situ and in UHV using ambient-pressure photoemission and X-ray absorption spectroscopy techniques [1,2]. At water pressures above 10<sup>-5</sup> Torr a significant pressure-dependent decrease in the temperature for dissociative desorption was observed for both amino acids on Cu{110}[3]. On Pt{111}, on the other hand, desorption temperature does not depend significantly on the presence of water vapor. The most likely reaction mechanism of decomposition involves dehydrogenation induced by O and/or OH surface species resulting from the dissociative adsorption of water on Cu{110}, but not on Pt{111}.

The linear relationship between the inverse decomposition temperature on Cu{110} and the logarithm of water pressure enables determination of the activation energy for the surface reaction, between 213 and 232 kJ/mol, and a prediction of the decomposition temperature at the solid-liquid interface by extrapolating towards the equilibrium vapour pressure. Such experiments near the equilibrium vapour pressure provide important information about

elementary surface processes at the solid-liquid interface, which can neither be retrieved under ultra-high vacuum conditions nor from interfaces immersed in a solution.

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11:00am **IS+AS+SS-TuM10 STM Tip Catalyzed Adsorption of Thiol Molecules and Functional Group-Selective Adsorption of Bi-Functional Molecule Using This Catalysis.** *Y.H. Min, S. Kim, S.J. Jung, Y.-S. Youn, Korea Advanced Institute of Science and Technology, Republic of Korea, D.H. Kim, Daegu University, Republic of Korea, E.H. Park, Korea Advanced Institute of Science and Technology, Republic of Korea*

In this study, in contrast with cases in which Scanning Tunneling Microscopy (STM) tip-induced reactions were instigated by the tunneling electrons, the local electric field, or the mechanical force between a tip and a surface, we found that the tungsten oxide (WO<sub>3</sub>) covered tungsten (W) tip of a STM acted as a chemical catalyst for the S-H dissociative adsorption of phenylthiol and 1-octanethiol onto a Ge(100) surface. By varying the distance between the tip and the surface, the degree of the tip-catalyzed adsorption could be controlled. We have found that the thiol head-group is the critical functional group for this catalysis and the catalytic material is the WO<sub>3</sub> layer of the tip. After removing the WO<sub>3</sub> layer by field emission treatment, the catalytic activity of the tip has been lost.

3-mercapto isobutyric acid is bi-functional molecule which has two functional groups, carboxylic acid group and thiol group, at each end. 3-Mercapto Isobutyric Acid adsorbs at Ge(100) surface only through carboxylic acid group at room temperature and this adsorption was enhanced by the tunneling electrons between a STM tip and the surface. Using this enhancement, it is possible to make thiol group-terminated surface where we desire. On the other hand, surprisingly, the WO<sub>3</sub> covered W tip of STM was found to act as a chemical catalyst to catalyze the adsorption of 3-mercapto isobutyric acid through thiol group at Ge(100) surface. Using this catalysis, it is possible to make carboxylic acid group-terminated surface where we want. This functional group-selective adsorption of bi-functional molecule using the catalysis may be used in positive lithographic methods to produce semiconductor substrate which is terminated by desired functional groups.

Min, Y. H.; Jung, S. J.; Youn, Y. -S.; Kim, D. H.; Kim, S. *J. Am. Chem. Soc.* **2010**, *132*, 9014.

11:20am **IS+AS+SS-TuM11 CO<sub>2</sub> Capture in Aqueous Monoethanolamine Solutions: Role of the Solution Interface Investigated with X-ray Photoelectron Spectroscopy.** *T. Lewis, University of California, Irvine, B. Winter, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, M. Faubel, Max-Planck-Institut für Dynamik und Selbstorganisation, Germany, J.C. Hemminger, University of California, Irvine*

Aqueous monoethanolamine (MEA) solutions are commonly used to capture CO<sub>2</sub> emitted into the atmosphere from industrial processes. It is likely that interactions between MEA and CO<sub>2</sub> at the aqueous solution surface are important to this process, yet surprisingly very few studies have explicitly addressed the role of the solution-gas interface. In the present study, interfacial chemistry of CO<sub>2</sub> capture is studied by surface sensitive photoelectron spectroscopy measurements from a liquid microjet of CO<sub>2</sub>-reacted MEA solutions with carbon loadings of 0.1 to 0.9 mol/mol. These experiments determine the spatial distribution of MEA and reaction products into the solution as a function of CO<sub>2</sub> loading. Results show that neutral MEA exhibits a propensity for the solution surface, whereas protonated MEA and reaction products prefer bulk solvation, suggesting enhanced reactivity at the solution interface, especially at high CO<sub>2</sub> loading. These observations indicate that a detailed understanding of the chemistry of CO<sub>2</sub> at the liquid/vapor interface and interface to bulk transport of the products will be important in understanding CO<sub>2</sub> capture.

11:40am **IS+AS+SS-TuM12 Fundamental Aspects of Organic Heterostructure Formation Examined using Supersonic Molecular Techniques and In Situ Real Time X-ray Synchrotron Radiation.** *E.R. Kish, T.V. Desai, A.R. Woll, J.R. Engstrom, Cornell University*

Over the past several years significant advances have been made concerning our understanding of the growth of crystalline small molecule organic thin films consisting of a single component. An important challenge in organic electronics, photonics and photovoltaics is to develop and improve methods to integrate both *p*-type and *n*-type small molecule organic semiconductors into the same device microstructure. Thus, developing an understanding of

the molecular scale events that lead to heterojunction formation is essential in these systems consisting of multiple components. Here we report on our examinations of the nucleation, growth, and dynamics of adsorption of a *n*-type organic semiconductor, *N,N'*-ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C<sub>13</sub>), on SiO<sub>2</sub> surfaces modified by self-assembled monolayers (SAMs) and on a pre-deposited monolayer of pentacene (a *p*-type semiconductor) using supersonic molecular beam techniques, *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy. From real-time x-ray scattering we find that PTCDI-C<sub>13</sub> exhibits prolonged layer-by-layer growth for approximately the first 10 monolayers (MLs) of deposition on all three SAMs examined. Concerning the kinetics of growth we find that the adsorption probability of PTCDI-C<sub>13</sub> on itself is similar to that observed on two SAMs that possess aromatic endgroups, but it differs significantly to that observed on a relatively short, methyl-terminated SAM. These differences could reflect mechanisms such as direct molecular insertion of PTCDI-C<sub>13</sub> into either the existing PTCDI-C<sub>13</sub> film, or the longer chain SAMs with aromatic endgroups. Concerning growth in the submonolayer regime, we find that nucleation is homogeneous, and that the absolute density of islands depends on the nature of the surface, while the relative change of the island density with increasing growth rate is essentially independent of the underlying SAM. From the latter we find that a critical island size of a single molecule of PTCDI-C<sub>13</sub> can describe all the data. Finally, we will discuss our most recent results concerning the growth of heterostructures composed of a few to several monolayer stacks of PTCDI-C<sub>13</sub> and pentacene. In this work we find that PTCDI-C<sub>13</sub> grows in a smooth layer-by-layer fashion on pentacene, but the opposite is not true—pentacene grows in a purely 3D mode when deposited on PTCDI-C<sub>13</sub>. We will discuss the implications of this observation concerning the growth of organic heterostructures for applications in electronics, photonics and photovoltaics.

# Tuesday Afternoon, November 1, 2011

Applied Surface Science Division

Room: 102 - Session AS-TuA

## Imaging and 3D Chemical Analysis - Part II

Moderator: W. Stickle, HP ADL Corvallis

2:00pm **AS-TuA1 Integration of an External Cavity Quantum Cascade Laser Into a Scattering-Type Infrared Scanning Near-Field Optical Microscope**, *A.S. Lea, M.S. Taubman, M.C. Phillips*, Pacific Northwest National Laboratory, *M. Raschke*, University of Colorado, Boulder

Molecular nanostructures, polymer and supramolecular assemblies, proteins, biomembranes, correlated systems, and many other natural and synthetic materials gain their unique functionalities from intra- and intermolecular interaction and electron correlations on mesoscopic length scales of 10's of nm. Gaining a molecular level understanding of the materials structure and function has remained a major experimental challenge. This is due to the lack of experimental techniques that can routinely provide a chemically specific spectroscopic identification with simultaneous nanometer spatial resolution on the relevant length scale associated with the size and interactions of the molecular building blocks: within the 10 – 100 nm range. We have developed an instrument for spectroscopic infrared vibrational near-field nanoimaging capable of ultrahigh spatial resolution down below 10 nm, vibrational spectral information in the 14 to 2 um range, sensitivity down to the molecular level, and applicability under ambient and environmental conditions. There are few instruments that can provide near field IR nanoimaging at high resolution, but except for the aforementioned instrument, none are broadly tunable over a large spectroscopic range nor has resolution that approaches 10nm.

We are integrating a Quantum Cascade Laser to the new instrument as a complementary IR light source to the femtosecond OPO chain. QCLs are a monopolar semiconductor laser devices that can be fabricated to cover significant regions of the mid IR spectrum, specifically 3.5 to 20 microns. Moreover, these devices work extremely well in the molecular fingerprint region (8 to 12 microns), which will be of particular use in this instrument as this is where many fundamental vibrational bands are found, where MCT IR detectors work best, and the region is relatively free from water interference. The rapid scanning capabilities of External Cavity QCLs (ECQCLs) in the 100s of Hz, will allow IR spectra to be taken point by point across the sample, allowing rapid spectral data coverage. This is to be compared with the Hz-rate scanning of the OPO chain. The second significant advantage of QCL incorporation will be its ease of use (permitting wide-spread usage), low cost and ruggedness. This presentation will cover the integration of an ECQCL into the existing scattering-type IR scanning near-field optical microscope and demonstrate its ability to provide spatially resolved IR spectroscopic signatures on a sub-100nm scale. Ultimately, we anticipate this instrument will be able to provide chemical binding information of molecular adsorbates on nanostructured materials.

2:20pm **AS-TuA2 An Investigation Into the Aging of Paintings using Surface Analysis Techniques**, *T.S. Nunney*, Thermo Fisher Scientific, UK, *J.J. Boon*, AMOLF, Netherlands, *E.S.B. Ferreira*, Swiss Institute for Art Research (SIK-ISEA), Switzerland

The understanding of the processes involved in the aging of artworks is of considerable importance in maintaining these pieces for future generations. Delamination of paint layers, chemical reactions of constituents in and between paint layers, interactions with the material that the paint was applied to, and the influence of the environment on the works can all have an effect on their appearance. By understanding these processes, conservators can attempt to retain the appearance as the artist intended.

Surface analysis has been used to investigate a cross-section sample taken from "Autumn in Schwand" (1906) by Cuno Amiet (1868-1961). The painting has become lighter in certain areas, and the cause of this was investigated. EDS analysis indicated that a higher proportion of lead had accumulated near the surface of the outer paint layer. XPS imaging of the sample in conjunction with multivariate statistical analysis of the data allows the chemical state of the individual components to be distinguished, from lead carbonate (or "lead white" pigment) to the lead soaps that are causing the change in the appearance of the painting, and the copper, chromium and arsenic pigments that form the paint layers. These analyses were compared with spectra from reference pigments to identify the original paints used. Further investigation using Raman and FTIR microscopy was used to complete the analysis.

2:40pm **AS-TuA3 Probing Insect Tissue by NEXAFS Imaging: A Chemical Characterization of Cuticle from an African Flower Scarab (*Eudicella gralli*)**, *J.E. Baio*, University of Washington, *C. Jaye*, National Institute of Standards and Technology, *E. Sullivan*, Woodland Park Zoo, *D.A. Fischer*, National Institute of Standards and Technology, *D.G. Castner*, *T. Weidner*, University of Washington

Insect cuticle is a matrix of structural proteins and long chain polymers of chitin. The chemical composition of the cuticle is dictated by the biomechanics of the insect. Regions of the exoskeleton where extra stiffness is required - this matrix become mineralized and form sclerites. Elastic portions of the cuticle are rich with pliable structural proteins. While engineers have set out to copy these biomineralization processes and design materials that mimic the extraordinary structural capabilities of these exoskeletons – a complete understanding of the structure of this chitin/protein/mineral matrix does not currently exist. In this study, we set out to spatially resolve the chemistry, at the cuticle surface, of an African Flower Scarab (*Eudicella gralli*) by near edge x-ray adsorption fine structure (NEXAFS) imaging. The NEXAFS images are produced by a new parallel process magnetic field electron yield optics detector, and a full field incident soft X-ray beam on the sample. The rapid parallel process magnetic field electron yield optics detector (LARIAT:Large Area Imaging Analytical Tool) produces a series of two-dimensional NEXAFS spatial images as the incident soft X-ray energy is scanned above a K or L absorption edge. A spatially resolved view of cuticle surface chemistry was created by mapping spectral features within the carbon (270-370 eV), nitrogen (380-430 eV), and oxygen (520-580 eV) K-edge spectra. Distributions of protein and chitin rich regions around the beetle were defined by changes in intensity of  $\pi^*$ (284.5 eV) and C-H\* (290 eV) within the C K-edge spectra. Regions of high mineralization were observed around the edges of the beetle's head and were assigned by tracking the intensities of the calcium (330-360 eV) and iron (700-740 eV) L-edges. These images also showcase the strengths of NEXAFS imaging, which unlike other photoelectron spectroscopy modalities, allowed us to collect high quality spectra over a large field of view (12 mm x 18 mm ) at a range of x-ray incidence angles, with little beam damage to the tissue.

3:00pm **AS-TuA4 Surface Cleaning of Organic and Inorganic Materials with Argon Cluster Ion Beams**, *A.E. Wright*, *P. Mack*, *O. Greenwood*, Thermo Fisher Scientific, UK

Surface analysis of many materials can be impeded by the presence of contaminant substances at the surface. Signals from these contaminants can dominate a photoelectron spectrum, leaving little contribution from the underlying material of interest. Spectroscopic analysis of contaminated samples can be a considerable challenge in surface science, so methods of cleaning samples are of some importance. One common method of removing contamination *in vacuo* is argon ion sputtering, which can be effective at removing surface materials. Damage to the underlying material can be substantial with argon ions, however, particularly at high impact energies. Ion impacts can disrupt polymer structures and reduce inorganic oxides, so that the surface after cleaning does not closely resemble the intact material.

The recent development of argon cluster ion beam sources promises significant improvements in depth profiling of soft materials. Cluster beams can offer exceptionally gentle sputtering, and so may be ideally suited to removal of contaminants and surface modifications from a variety of samples.

In this presentation, we evaluate the utility of argon cluster ions for the surface cleaning of various materials, in combination with the Thermo Scientific ESCALAB250Xi surface analysis instrument for characterisation of the samples. The results of gas cluster profiling on polymeric and inorganic materials will be presented, with spectroscopic and imaging analyses showing the benefits of this method.

4:00pm **AS-TuA7 Structure Determination of Heterogeneous Materials through 3D Imaging using XPS and Multivariate Analysis**, *K. Artyushkova*, The University of New Mexico, *S.J. Coultas*, *S.J. Hutton*, *A.J. Roberts*, Kratos Analytical Inc.

The sputtering of solids with ion beams followed by analysis with photoelectron spectroscopy has been widely used as it offers a powerful strategy for the in-depth characterization of complex inorganic materials. The combination of imaging techniques with depth profiling to create three-dimensional information is an obvious and exciting extension of these experiments. Recent introduction of cluster ion beams, such as coronene,

into XPS instrumentation offers capabilities in quantifying the chemical and molecular gradients in the near surface region of soft materials, such as polymers and biomaterials. XPS data can be acquired as a function of sputter depth into organic materials while maintaining molecular integrity.

There are only a handful number of studies combining XPS imaging and depth sputtering. One of the biggest problems when dealing with 3D imaging data sets is visualizing the lateral distribution of chemical moieties as a function of depth. When multispectral images are acquired at each sputtered depth, four-dimensional datasets can result with a full spectrum acquired at each voxel of the space. These datasets represent a huge amount of data which can only be interpreted with assistance of Multivariate Analysis.

In this research we report on application of various types of MSA methods such as two-step PCA and two-step MCR-ALS, PARAFAC, MFA, Tucker and 3D MCR-ALS to multispectral XPS imaging data acquired as a function of sputtering depth for different heterogeneous biomaterials and polymers. The component images extracted from MSA, which show the spatial distribution of the various chemical components, will be visualized in 3D individually or together representing an overall chemistry of individual layers.

**4:20pm AS-TuA8 Interface Orientation Dependent Field Evaporation Behavior in Multilayer Thin Films, J.G. Brons, University of Alabama, A.A. Herzing, K.L. Henry, I.M. Anderson, National Institute of Standards and Technology, G.B. Thompson, University of Alabama**

Intermixing between thin film layers can alter mechanical and thermal transport properties, phase stability and growth textures. Quantification of the degree of intermixing is crucial to identify the mechanisms of intermixing and their scaling effect on properties as listed previously. Atom probe tomography has received considerable attention for this type of characterization because of its ability to identify and provide reconstructions of atoms with near atomic spatial 3D resolution. In general, these atom probe reconstruction algorithms assume a constant evaporation field across the surface of the specimen. In reality, chemical inhomogeneity (i.e. discrete interfaces) modulates the evaporation field at the specimen surface. This introduces reconstruction artifacts and degrades the spatial resolution of the atom probe tomography technique. Multilayer thin films provide ideal specimen geometries to measure and quantify these artifacts since thin films can be deposited with near atomic layer precision and can exhibit large planar surfaces with various degrees of intermixing across the interfaces. A series of Fe/Ni and Ti/Nb multilayers with bilayer repeat distances of 4 nm have been sputter-deposited onto n-doped Si [001] substrates. The multilayers were annular focus ion beam milled into the required needle-shaped geometry for the atom probe analysis with the film interfaces oriented with the bilayer chemical modulations parallel and perpendicular to the specimen apex. This was done to compare field evaporation behavior at these limiting geometries. The atom probe compositional profiles were then compared to Electron Energy Loss Spectroscopy (EELS) compositional profiles to determine the fidelity of the reconstructions through cross-comparison microscopy. The best agreement between the profiles was seen for Fe/Ni (similar field strengths) in a perpendicular-to-the-apex orientation.

**4:40pm AS-TuA9 Atom Probe Tomography and Spectroscopic Analysis of Wide Bandgap Nanostructures, N. Dawahre, G. Shen, W. Baughman, S. Balci, S. Wilbert, N. Harris, L. Butler, S. Kim, P. Kung, University of Alabama**

Wide bandgap ZnO based semiconductors are materials of great importance in an increasingly large number of optoelectronic devices for energy applications, including high efficiency low cost photovoltaics, solid-state lighting, ultraviolet light emitting and laser diodes, transparent electronics, transparent conducting windows that can be a potentially cheaper and more abundant substitute to ITO for photonic devices, and higher performance scaffold than TiO<sub>2</sub> in sensitized solar cells. The material's wide bandgap, large exciton binding energy, and piezoelectricity can now be exploited at the nanoscale through the realization of nanobelts, nanoribbons and nanowires, leading to a dramatically expanded range of applications (e.g. chemical sensors and mechanical energy harvesting devices, etc). Enhancing our understanding of the chemical purity of ZnO nanostructures and understanding of the interfaces in ZnO based nano-heterostructures with atomic resolution is essential in order to enable the development of novel devices while further improving the performance of existing ones.

In this talk, we report the use and development of atom probe tomography (APT) in order to image the chemical composition of well aligned ZnO nanowires synthesized by thermal chemical vapor deposition and its relation to other material spectroscopic characteristics. The ZnO nanowires used were on various substrates, including sapphire, GaN and Si. The nanowires were single crystalline, 0.5-20 um long with a diameter controllable from 50 to 150 nm and a density on the order of 10<sup>8</sup> per cm<sup>2</sup>.

We subsequently discuss the sample preparation techniques employed and the influence of various APT measurement parameters on the quality of the data collected. Atoms probe tomography (APT), which combines a field ion microscope and a time-of-flight mass spectrometer, is an analytical technique which is unmatched in identifying composition at the atomic scale and in 3D. However, proper interpretation of the APT data required thorough analysis of the mass spectra. Data analysis was also carried out in correlation with the nanowire synthesis conditions (e.g. carrier gas and dopant) and with other characterization techniques aimed at assessing the nanowire optical and electrical properties. These included high resolution transmission electron microscopy along with energy dispersive spectroscopy mapping, confocal Raman spectroscopy and imaging, confocal photoluminescence and imaging, as well as terahertz time domain spectroscopy.

**5:00pm AS-TuA10 Probing 3D-Semiconductor Structures, Vandervorst, IMEC, Belgium INVITED**

The trends in advanced semiconductor devices and technologies call for the ability to probe compositional and impurity distributions with a depth resolution approaching near-atomic resolution. At same time, quantitative interpretation is of utmost importance in particular in multilayer structures and at interfaces such as local silicide composition and phase, interfacial interactions high k metal gate, etc.. At the same time one must admit that the advent of nanoscale devices and three-dimensional structures like Finfets, nanowires necessitates techniques which provide 3D-resolution. In this paper we will discuss recent approaches in extracting local 2D, 3D information on dopant distributions, carrier distribution, defects in thin dielectrics, phase and composition analysis, detection of small voids in ultra narrow interconnect lines (> 15 nm) as well as in (large, > 50 micron!) Cu-interconnects (TSV's).

For nanoscale 1D and 2D characterization we presently rely on concepts such as EXLE-SIMS for ultra high depth resolution dopant profiling, SSRM for 2D- carrier analysis, C-AFM for dielectrics, (S)TEM (+ELNES, EDX, HAADF) for quantitative composition analysis. 3D-characterization represents a serious challenge and one must rely on concepts like the tomographic Atom Probe to extract 3D-composition analysis on the nm-scale or Tomographic TEM. We will show examples for both cases and address the issues of Atom Probe in particular as the latter, although very appealing, does contain many artifacts as well. The latter are linked to sample preparation, laser-tip interaction, and reconstruction artifacts as well as issues inherently linked to instrument performance (mass resolution, sensitivity,...) and underlying physics (linked to sample heterogeneity). For analysing 3D-dopant distributions in Finfets, this can be complemented with tomographic SSRM and SIMS through Fins.

For back-end applications, the detection voids in narrow Cu-lines (15-30 nm) can be done using EDX whereas their analysis in the very large Cu TSV's requires sophisticated ion milling approaches (plasma based FIB, slcie and view) as excessive milling times and surface topography evolution (curtaining) can hide the required information.

**Helium Ion Microscopy Focus Topic  
Room: 106 - Session HI+AS-TuA**

**Basics of Helium Ion Microscopy**

**Moderator:** A. Götzhäuser, University of Bielefeld, Germany, V.S. Smentkowski, GE-GRC

**2:00pm HI+AS-TuA1 Principles of Helium Ion Microscopy, J.A. Notte, L. Scipioni, L.A. Stern, Carl Zeiss NTS INVITED**

The Helium Ion Microscope (HIM) consists of an interesting blend of long established technologies and recent state of the art engineering designs that enable superior charged particle scanning microscopy capabilities. They are capable of providing sub-nanometer spatial resolution with remarkable surface information and a unique ability to image insulating samples. HIMs share many similarities with Scanning Electron Microscopes (SEMs), but also embody new principles that uniquely differentiate HIM hardware and applications from traditional SEMs.

The most significant hardware difference of the HIM compared to SEM is the ion source. On the macroscopic scale the source appears very similar to a standard electron field emission source. However, the detailed tip geometry allows for much higher electric fields to be produced in the vicinity of the tip than what is found in traditional SEM field emission sources. The higher field enables ionization of the neutral helium gas which surrounds the tip, producing the needed helium ion beam. In addition to the high electric field requirement, it is necessary to keep the tip and surrounding imaging gas at cryogenic temperatures. The implementation of

source cryogenics while operating the tip at ~ 35 keV, and also maintaining mechanical motion for both source translation and tilting, introduces significant engineering challenges in the design of a HIM.

Due to fundamental differences between helium ion and electron interactions with the sample under observation, the HIM is capable of producing images that are significantly different from those produced by traditional SEM. Since the entire electron population created due to an incident helium ion is of very low energy, only those electrons near the point of helium incidence are capable of escaping from the sample, resulting in images that are rich with surface information and possess superior spatial resolution. Due to the much higher secondary electron yield associated with helium bombardment of a sample relative to electron bombardment, and the fact that the incoming particles are positively charged, the net charge state of the sample is always positive, unlike the SEM case. Furthermore, due to the strong affinity of a helium ion to capture an electron, the net charge on the sample always exists as a surface charge. The positive surface charge can be easily neutralized with an electron flood gun, thus enabling charge free imaging on highly insulating samples. These various unique imaging principles make the HIM a versatile and unique imaging instrument.

**2:40pm HI+AS-TuA3 Design and Performance of a Near Ultra High Vacuum Helium Ion Microscope, R. van Gastel, University of Twente, The Netherlands, L. Barriss, J.A. Notte, Carl Zeiss NTS, G. Hlawacek, University of Twente, The Netherlands, L. Scipioni, A.P. Merkle, D. Voci, Carl Zeiss NTS, C. Fenner, L Vestus Energy Inc., H. Zandvliet, B. Poelsema, University of Twente, The Netherlands**

The advent of He Ion Microscopy (HIM) as a new technique to image materials and microstructures has enabled a new look at materials that is based on the interaction of swift light ions with matter, as opposed to that of more commonly used high (and low) energy electrons [1]. Initial Carl Zeiss Orion® He Ion Microscope instruments have demonstrated high-resolution imaging, combined with great surface sensitivity, the ability to neutralize charge very efficiently, and with enhanced materials contrast when ion induced secondary electrons are used for imaging. The use of Rutherford backscattered ions to form images has provided a new imaging modality that emphasizes differences in elemental composition and it can also be used to probe samples in-depth.

The HIM provides obvious benefits in terms of novel modes of contrast, surface sensitivity, lateral resolution, depth of field and charge compensation. To achieve ultimate performance, the chamber vacuum of the existing platform may be improved. For instance, carbon deposits due to beam interaction are readily seen due to the surface sensitivity of the technique. At sufficiently high current densities the sharply focused He ion beam may very efficiently decompose or cross-link residual hydrocarbons that are present in the instruments vacuum, more so than an electron beam in a SEM setup. Not only can this obscure a clear view of the sample, thereby negating the benefits of the small spot size, it also limits the available acquisition time for spectroscopic measurements. In addition to this, some materials (Au in particular) have yielded unexpectedly high sputtering rates. On the one hand, this has proven extremely useful in the field of nanopatterning for sensors, plasmonics or other device fabrication applications at the sub-10nm level when operating at high doses. On the other hand, it is undesirable when the instrument is used for materials characterization.

In this presentation we will discuss the basic considerations that went into the design of a Near-UHV (NUHV) Orion Plus® He Ion Microscope. We will detail how the improved vacuum level is anticipated to alter those processes that are directly relevant to the imaging performance of the instrument such as beam interaction in the surface region and the emission of secondary electrons. First applications that the instrument was used for will be highlighted and its impact in the areas of surface physics, notably catalysis, corrosion, and other research areas that require increased imaging sensitivity, both laterally and in depth, will be discussed.

#### References

[1] B. Ward, J. Notte, and N. Economou, *J. Vac. Sci. Technol.* 24, 2871 (2006).

**3:00pm HI+AS-TuA4 Sub-10 nm Scanning Helium Ion Beam Lithography, K. van Langen, E.W.J.M. van der Drift, Delft University of Technology, Netherlands, E. van Veldhoven, D.J. Maas, TNO, Netherlands, P.F.A. Alkemade, Delft University of Technology, Netherlands**

Since the launch of the novel sub-nanometer helium ion microscope by Zeiss / Alis in 2006 nanofabrication with this tool has gained a lot of interest [1]. Key characteristic in this matter is the directional interaction of the helium ion with matter with negligible backscattering. In ion milling it enables very steep structuring when compared to the Ga<sup>+</sup> ion equivalent [2]. In a similar comparison helium ion beam-induced deposition in a precursor gas ambient yields tall and smooth nanostructures [3], partially also because the sputtering by helium ions is at least an order of magnitude lower than by gallium ions.

The present contribution deals with scanning helium ion beam lithography (SHIBL). Thusfar two initial SHIBL studies on hydrogensylsesquioxane (HSQ) resist were reported [4,5]. In the present work performance of SHIBL is compared with state-of-the-art electron beam lithography (EBL). As resist materials we explored HSQ, polymethylmethacrylate (PMMA), and the inorganic resist of aluminumoxide. The latter material choice is motivated by the need for enhanced mask selectivity in pattern transfer in the sub-10-nm area.

The results for HSQ and PMMA can be summarized as:

- smallest feature size of 5 nm, equivalent to the best EBL performance [6]
- clear pattern densities up to 10 nm full-pitch, which is better than in EBL
- sensitivity 1-2 orders of magnitude better than in EBL.

As for the inorganic resist, 5-nm features have been realized.

In a semi-quantitative and comparative approach the results will be explained and future prospects will be outlined.

1 R. Hill, F.H.M. Faridur Rahman, *Nucl. Instr. and Meth. A* (2010), doi:10.1016/j.nima.2010.12.123, in press

2 L. Scipioni, D. C. Ferranti, V. S. Smentkowski, R.A. Potyrailo, *J. Vac. Sci. Technol. B* (2010) 28: C6P18

3 P. Chen, E. van Veldhoven, C.A. Sanford, H.W.M. Salemink, D.J. Maas, D.A. Smith, P.D. Rack, and P.F.A. Alkemade, *Nanotechnol.* (2010) 21: 455302

4 V. Sidorkin, E. van Veldhoven, E. van der Drift, P. Alkemade, H. Salemink, D. Maas, *J. Vac. Sci. Technol. B* (2009) 27: L18

5 D. Winston, B.M. Cord, B. Ming, D.C. Bell, W.F. DiNatale, L.A. Stern, A.E. Vladar, M.T. Postek, M.K. Mondol, J.K.W. Yang, K.K. Berggren, *J. Vac. Sci. Technol. B* (2009) 27: 2702

6 H. Duan, D. Winston, J.K.W. Yang, B.M. Cord, V.R. Manfrinato, and K.K. Berggren, *J. Vac. Sci. Technol. B.* (2010) 28: C6C58

**4:00pm HI+AS-TuA7 Contrast Performance in Helium Ion Microscopy, D.C. Bell, Harvard University INVITED**

In order to achieve ultra high resolution imaging with secondary electron imaging, it is critical that the electric potential of the specimen surface is well controlled. For electrically conductive samples this can be achieved by simply grounding the specimen. However, imaging of electrically insulating specimens can provide challenging or impossible to image due to uncompensated charge resulting from the electron or ion beam interaction with the specimen surface. The main reason for the uncompensated charge is that the insulating specimen has insufficient conductivity through mobility of either electrons or holes to quickly restore the neutrality of the scanned area. The buildup charge causes significant deflection and distortion of the ion or electron beam. Which is more appropriate, to use charge compensation with high kV helium ions or employ a low kV SEM image to obtain the required surface information? This paper will present a systematic examination of the surface information provided by both techniques, including SEM charge compensation mechanisms.

One key advantage of the Helium Ion Microscope technology in the case of imaging highly charging specimens is the electron flood gun can be utilized to neutralize the positive charge buildup and facilitate high-resolution imaging. A flood gun is used to charge the surface to a negative potential (using electrons as the neutralizing particles). When utilizing the electron flood gun, the electron beam and He ion beam are synchronized and adjusted with respect to one another, so that the low energy electrons are not interfering with the secondary electron imaging.

Some of our research from the past year has been surprising and may provide a foundation for a change in analysis techniques of different materials. The nature of the Helium ion beam interactions with the sample shows enhanced edge contrast which is especially useful for critical dimension measurements; one particularly interesting development is the imaging of non-conducting materials showing a contrast due to three apparent mechanisms simultaneously - atomic number, channeling contrast and a possible enhanced edge contrast. The advantages of Helium ion



microscopy is still being investigated and still are proving some exciting results.

5:00pm **HI+AS-TuA10 Helium Ion Beam Induced Deposition Examined using a 3D Monte Carlo Simulation**, *D.A. Smith, P.D. Rack*, University of Tennessee Knoxville, *P.F.A. Alkemade, H. Miro*, Delft University of Technology, The Netherlands

The growth of nanostructures has traditionally been dominated by electron beam induced deposition (EBID) or gallium ion beam induced deposition (Ga-IBID). While EBID provides smooth sidewalls and good resolution for nanopillar growth, the cross-section for dissociation is low and etching is difficult as sputtering is negligible. Ga-IBID is a relatively faster method of producing nanostructures, however it suffers from lower resolution, alters deposited materials, and leaves an etching residue. A new tool in this field has been recently explored: the helium ion beam microscope. This tool has been modified to perform IBID using high energy helium ions. It has been found that He-IBID combines the high resolution of EBID with the speed of Ga-IBID. Moreover, there is less implantation damage and minimal sputtering compared to Ga beams.

To examine this process, a 3-dimensional Monte Carlo simulator has been designed based on ion-solid-precursor interactions. This simulation system, named EnvisION, can provide useful knowledge of how user-controlled parameters can be optimized for highly efficient growth of nanostructures using this tool. In this work, an in-depth explanation of the simulation will be presented, including an example of its use examining the growth efficiencies of nanopillars grown on a silicon substrate using the (CH<sub>3</sub>)<sub>3</sub>Pt(CpCH<sub>3</sub>) precursor via He-IBID. Furthermore we compare how the morphology changes with dwell times, refresh time, precursor coverage and surface diffusion in order to span the range of growth regimes from mass-transport limited to reaction-rate limited deposition. The simulated morphologies predicted using the EnvisION simulator are compared to experimentally grown pillars to validate the simulation.

5:20pm **HI+AS-TuA11 TEM Specimen Preparation with Light Ions**, *L. Giannuzzi*, L.A. Giannuzzi & Associates LLC

Much research with light energetic ions such as He<sup>+</sup> and Ne<sup>+</sup> from gas field ionization sources has focused on imaging and nano-machining. It is a natural progression to question to the viability of TEM specimen preparation using these light ions. Of vital importance for TEM specimen preparation quality is the understanding of surface ion implantation and amorphization damage. Theoretical calculations using SRIM indicate that there may be a damage trade off between vacancy formation, ion range, and dose. That is, the range of light ions is much greater than conventional heavy ions (e.g., Ga<sup>+</sup>), and can indeed penetrate directly through a TEM specimen. While this may indicate the possibility of light ions damaging the entire TEM specimen thickness, light ions produce far less vacancies per ion compared to heavy ions for the same dose. However, since the sputter yield of light ions is smaller than heavy ions, a larger dose of light ions may be necessary to achieve sufficient material sputtering. This theory will be supplemented with experimental results.

5:40pm **HI+AS-TuA12 The Possibilities of the HIM for Imaging and Nanopatterning of EUVL Masks**, *D.J. Maas, E. van Veldhoven, N.B. Koster*, TNO, Netherlands, *P.F.A. Alkemade, E.W.J.M. van der Drift*, Delft University of Technology, Netherlands

Although Helium Ion Microscopy (HIM) was introduced only a few years ago [1], many new application fields are emerging. Key issue is the directional interaction of the primary helium ion beam with the sample at and just below its surface with negligible backscattering. The sub-nanometer sized probe of the 10-35 keV ion beam generates Secondary Electrons (SEs) that have a typical energy between 0 and 20 eV. Taking all together the SE signal stems from an area that is very well localized around the point of incidence of the primary beam. This makes the HIM well-suited for both high-resolution imaging as well as high resolution nanofabrication [2]. We explore the possibilities to use the HIM simultaneously for imaging and nano patterning of EUVL masks.

The HIM is a high-resolution surface imaging tool. In practice, the optimum dose for imaging is a balance between maximizing S/N ratio, while minimizing sample damage. Imaging work at TNO van Leeuwenhoek Laboratory (VLL) [3] focuses at sensitive materials such as e.g. DUV and EUV resists and EUV masks, which are difficult to image in a SEM due to their charging behavior. An electron flood gun in the HIM offers effective charge cancellation, which enables high-resolution imaging of insulation structures and for pin pointing defects on a EUV reticle. In this presentation we will show images of particles down to 5 nm on reticles.

Furthermore, to explore the possibilities of the helium ion microscope as a nanofabrication tool, the HIM at the TNO VLL is equipped with a pattern generator and a gas injection system (GIS). This presentation will show our latest nano structuring results made with Helium Ion Beam Induced

Processes: deposition and etching. It is expected that the unique capabilities of the HIM in combination with the GIS are suited for EUV mask repair. These capabilities offer the possibility of circuit repair in the latest and smallest semiconductor technology nodes (beyond 22 nm). In both cases sub-surface damage due to scattered He ions is a matter of concern and topic of investigation. At this moment we are capable of etching 13 nm lines with 25 nm spacing on a EUV dummy mask with approximately 80 nm of TaN absorber. Furthermore we demonstrate Pt deposited lines of 13 nm width at a 16 nm spacing.

References

- [1] J. Morgan, J. Notte, R. Hill, and B. Ward, *Microscopy Today* 14, (2006) 24
- [2] D.J. Maas et al., *Proc. SPIE Vol. 7638, 763614* (2010) 1-8
- [3] <http://www.vanleeuwenhoeklab.com/>

## Nanometer-scale Science and Technology Division Room: 203 - Session NS+AS-TuA

### Frontiers in Nanoscale Imaging and Characterization Moderator: E.I. Altman, Yale University

2:00pm **NS+AS-TuA1 Proximity, Phonon in Nanometer Size Superconducting Nb Islands : A STM Study**, *S. Jeon*, Seoul National University, Republic of Korea, *H. Suh*, Samsung Advanced Institute of Technology, Republic of Korea, *Y. Oh, S. Kim, Y. Kuk*, Seoul National University, Republic of Korea, *M. Machida*, Japan Atomic Energy Agency, Japan

Despite successful macroscopic picture on a conventional superconductor niobium(Nb), not much were reported on nanometer scale objects. One may have to consider quantum mechanical size effect, fluctuation, and quantum phase slip in a nanometer scale superconducting object. In this study, quantum size effect of superconducting niobium(Nb) nano-islands grown on a tungsten(W) surface was investigated with scanning tunneling microscopy(STM) and scanning tunneling spectroscopy(STS). Various size (30nm ~ 200nm) of niobium islands were formed on a W(110) surface after making several layers of wetting layer. STS measurement at 4.2K showed that the Nb island have a BCS-like superconducting gap of about 2meV around the Fermi level. The critical temperature is much lower than that of the bulk value. In addition, We found spatial dispersion of DOS (density of states) outside of the superconducting gap. Spatially-resolved scanning tunneling spectroscopy(SR-STs) data taken inside and outside of the niobium islands reveal unique dispersion. That can be understood by quantum size effect based on Bogoliubov - de Gennes equation.

2:20pm **NS+AS-TuA2 Spin Excitation Spectroscopy**, *D. Eigler*, IBM Almaden Research Center

**INVITED**

The energies and relaxation times of spin excitations are traditionally measured using the classic spin resonance techniques, Nuclear Magnetic Resonance (NMR) or Electron Spin Resonance (ESR). The measurement of spatial variations of spin relaxation times is of profound practical importance as they are often used as the primary contrast mechanism in magnetic resonance imaging. It has been an outstanding challenge to extend the spatial resolution of these spectroscopies to the atomic scale. We have developed a new kind of spin spectroscopy, *Spin Excitation Spectroscopy*, that achieves this goal. Through a combination of inelastic tunneling spectroscopy and pump-probe techniques, we have extended the capability of the scanning tunneling microscope to interrogate both the energetics and dynamics of spin systems on the atomic scale. We anticipate that this will have application in a broad range of studies concerned with nanometer-scale magnetic systems, how they may be understood, and how they may be engineered to have a desired functionality.

Work done in collaboration with Cyrus Hirjibehedin, Andreas Heinrich, Christopher Lutz, Jay Gupta, Markus Ternes, Alexander Otte, Sebastian Loth and Bruce Melior

3:00pm **NS+AS-TuA4 Atom-Specific Interaction Quantification and Identification by Combined Scanning Tunneling and Atomic Force Microscopy**, *M.Z. Baykara, H. Mönig*, Yale University, *T.C. Schwendemann*, Southern Connecticut State University, *M. Todorovic, R. Perez*, Universidad Autónoma de Madrid, Spain, *E.I. Altman, U.D. Schwarz*, Yale University

On surfaces, forces extending into the vacuum direct the behavior of many scientifically and technologically important phenomena such as corrosion, adhesion, thin film growth, nanotribology, and surface catalysis. To advance our knowledge of the fundamentals governing these subjects, it

would be desirable to simultaneously determine a surface's structure, map electron densities, quantify force interactions, and identify chemical species. For example, in the case of a catalytically active surface, this would allow study of the role and effectiveness of surface defects such as vacancies, steps, kinks, impurities, and domain boundaries as active sites.

In this talk, we will show with the example of an oxygen/copper(100) surface phase that much of this information can be derived from combining the new method of three-dimensional atomic force microscopy (3D-AFM) [1,2], a variant of noncontact atomic force microscopy, with simultaneous 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. By combining experimental results with theoretical simulations, we will show how 3D data sets enable the site-specific quantification of force interactions and tunneling currents, how different chemical species can be imaged using different tips, different tunneling conditions, and different interaction mechanisms, and how structure-induced stress fields and their influence on the local chemical activity and topographical deformation can be studied.

[1] B. J. Albers et al., *Nature Nanotechnology* **4**, 307 (2009).

[2] M. Z. Baykara et al., *Advanced Materials* **22**, 2838 (2010).

**4:00pm NS+AS-TuA7 The Role of Surface States in Inelastic Electron Tunneling Into Metal Surfaces, P. Maksymovych, M.H. Pan, Q. Li, Oak Ridge National Laboratory**

A small fraction of electrons tunneling across a vacuum junction will undergo inelastic scattering, exciting surface phonons, molecular vibrations, magnons and plasmons in the contact leads. Although the study of surface phonons is a most straightforward inelastic electron tunneling spectroscopy (IETS) experiment, relatively few systematic studies have been done to date. One of the most surprising observations was that of atomic resolution in the IETS of Au(111) [1], and an equally intriguing variation phonon energy from 20 meV to 9 meV depending on the vertical stacking across the  $22\times 3$  reconstructed surface.

To investigate the origin of these effects on Au(111), we have carried out systematic IETS measurements using a home-built scanning tunneling microscope operating in the temperature range from 20K to 77 K. Particular emphasis was put on understanding of the role of the surface state in the electron-phonon coupling, judged from the intensity of the IETS signal and the energy of the observed vibrational modes.

We have found that largely independent of the measurement temperature, IETS spectra feature a broad peak centered around 18 meV, representing a weighted average of the phonon density of states within the Brillouin zone. Lower lying surface phonon bands (with energies from 7 to 9 meV) were resolved, but the majority of spectra are dominated by the peak at 18 meV, corresponding to the bulk phonon modes at the zone boundary. Although the spectrum remained largely unchanged across the surface, in contrast to earlier observations, the IETS intensity markedly dropped at the step edges. Furthermore, the IETS intensity exhibited long-range oscillations, the wavelength of which coincided with the Friedel oscillations of the surface state in the vicinity of the defects. Combined, the observations attest to the important role of the surface state in electron-phonon coupling [2], likely emphasizing the critical enhancement in the lifetime of hot electrons that tunnel into surface states relative to bulk states. We will also discuss the important role of tip effects in the IETS measurement. Tip-sensitivity may produce significant variations in the IETS spectrum across the herringbone reconstruction because of selectivity toward a particular phonon mode due to the convolution of the tip-surface interactions and heterogeneity of the surface state across the surface.

Research was conducted at the Center for Nanophase Materials Sciences and sponsored by the Division of Scientific User Facilities, U.S. Department of Energy.

[1] H. Gawronski, M. Mehlhorn, K. Morgenstern, *Science* **319** (2008) 930-933.

[2] Q. Li, P. Maksymovych, M. Pan et al, to be submitted (2011)

**4:20pm NS+AS-TuA8 2011 AVS Medard Welch Award Lecture - Inelastic Electron Tunneling Spectroscopy and Imaging of Single Molecules, W. Ho\*, University of California, Irvine INVITED**

The transformation of matter invariably involves energy transfer and redistribution. By probing matter and its coupling to external perturbations at the atomic scale with the scanning tunneling microscope (STM), it is possible to gain a broad range of new knowledge that would be difficult to

achieve by other techniques. Through high precision measurements of inelastic phenomena inside single molecules with the STM, chemical and physical properties of molecules are obtained by probing their response to electrons, photons, and an external magnetic field. The STM is used to measure the electronic and vibronic states, vibrational and spin excitations, and optical transitions in single molecules. New features emerge when measurements are carried out at increasingly extreme conditions of vacuum, temperature, magnetic field, and pulse duration of light while maintaining the atomic-scale spatial resolution. The inelastic processes can result in nuclear motions such as molecular rotation, diffusion, conformational change, bond dissociation, and bond formation. By studying a wide range of systems from atomic hydrogen to large molecules such as metal porphyrins and phthalocyanines on metal and thin oxide surfaces, the new knowledge obtained by the STM can be applied to the understanding and advancement of numerous technologies such as chemical catalysis, information storage, nanophotonics, alternative energies, and environmental remediation. Underlying these longer range applications is the immediate gain in the fundamental scientific understanding of matter that can be derived from these studies.

**5:00pm NS+AS-TuA10 Two-Color Ultrafast-Laser-Assisted STM, A. Dolocan, D. Acharya, P. Zahl, P. Sutter, N. Camillone, Brookhaven National Laboratory**

Substrate-adsorbate charge transfer and carrier-mediated substrate-adsorbate energy transfer are central to photoinduced surface chemistry. To investigate fundamental links between surface electron dynamics and heterogeneous photocatalysis we are developing an ultrafast-laser-excited scanning tunneling microscopy approach to probing surface electron dynamics with simultaneous subnanometer spatial and subpicosecond temporal resolution. Historically, thermal effects associated with laser power variations have presented a major hurdle to progress. In particular, thermal load modulations due to optical interference have been a barrier to observing dynamics at timescales on the order of the temporal width of the laser pulses. In this talk we present results from a new two-color method that completely eliminates this interference. We will show results for two cases: (1) where the tip is retracted from the surface far enough to prohibit tunneling, and (2) where the tip is within tunneling range of the surface. A delay-modulation technique isolates the two-color photo-emission from concurrent one-color two-photon photoemission and the conventional tunneling current, and also enables subpicosecond time-resolved detection of the photoexcited surface electrons. Advantages of the two-color approach are highlighted by comparison with the one-color case where optical interference causes current modulations that are orders of magnitude larger than the desired signal. The two-color approach represents an important step toward the ultimate goal of simultaneous subnanometer and subpicosecond measurement of surface electron dynamics.

**5:20pm NS+AS-TuA11 High Precision local electrical Probing: A New Low Temperature 4-Tip STM with Gemini UHV-SEM Navigation, B. Guenther, A. Bettac, M. Maier, M. Oertel, Omicron NanoTechnology, Germany, F. Matthes, C.M. Schneider, Forschungszentrum Juelich, Germany, A. Feltz, Omicron NanoTechnology, Germany**

A major challenge in the development of novel devices in nano- and molecular electronics is their interconnection with larger scale electrical circuits required to control and characterize their functional properties. Local electrical probing by multiple probes with STM precision can significantly improve efficiency in analyzing individual nano-electronic devices without the need of a full electrical integration. Among a very few commercial approaches, the Omicron *UHV NANOPROBE* has been established as a suitable instrument for local electrical probing in UHV on nano-structures down to structure sizes in the 10 nm range. The mayor technical requirements for such sophisticated instrumentation are:

- Rapid and simultaneous SEM navigation of four local STM probes on small structures
- Localization of nanostructures by high resolution SEM (UHV Gemini)
- Individual probe fine positioning by atomic scale STM imaging
- STM based probe approach for "soft-landing" of sharp and fragile probes and controlled electrical contact for transport measurements
- Preparation techniques towards sharp and clean and STM tips
- Suitable low noise signal re-routing for transport measurements with third party electronics

Although the *UHV NANOPROBE* has been successfully used for various applications, today's scientific requirements motivated the development of the next generation probing system. We will present the newly developed *LT NANOPROBE* which takes experimental capabilities one step further and opens up new research opportunities in nano-electronics, spintronics, and molecular electronics. Besides SEM/STM probe fine navigation and imaging, the excellent STM performance level of the *LT NANOPROBE*

\* Medard W. Welch Award Winner

expands applications to tunneling spectroscopy and even the creation or modification of nano-structures by an ultimately precise STM probe. The R&D project has been driven by the following major milestones:

- Operation at temperatures of  $T < 5$  K for STM imaging and STM based probing
- SEM navigation at base temperature  $T < 5$  K
- Simultaneous operation of STM and SEM at base temperature
- Thermal equilibrium of sample and probes for (i) extremely low thermal drift and electrode positioning accuracy in time and (ii) defined temperature of the local electrical contact and
- Performance and stability level of each individual STM Probe suitable for STM spectroscopy and atom manipulation

First evaluation measurements with the system installed at the Forschungszentrum Jülich will be presented: STM on Au(111) with pm stability, STS revealing the superconducting gap of a Nb tip with approx. 3meV gap size, and transport measurements on nanowires at  $T < 5$ K.

5:40pm **NS+AS-TuA12 Spin-Polarized VLEED: Experimental Access to the Spin-Dependent Surface Barrier**, *K. Wulff*, *A.B. Schmidt*, Westfälische Wilhelms-Universität Münster, Germany, *J. Braun*, Ludwig-Maximilians-Universität München, Germany, *M. Donath*, Westfälische Wilhelms-Universität Münster, Germany

The spin-dependent reflectivity of very-low-energy electrons from ferromagnetic surfaces has recently been utilized in a new type of electron spin detector [1,2]. The underlying effect is a result of electron scattering from a spin-dependent substrate potential as well as from a spin-dependent surface-potential barrier.

We present the first spin-polarized very-low-energy electron-diffraction (SPVLEED) measurements on a ferromagnetic system. Our data on Co/Cu(001) reveal a significant spin dependence of the reflected intensities that varies strongly with electron energy, polar and azimuth angle of incidence.

In these intensity vs. energy spectra  $I(V)$ , additionally, fine structures appear [3], which are caused by the surface-potential barrier. Their particular intensities and energy positions are very sensitive to the shape of the surface-potential barrier. On the vacuum side far from the surface, the barrier resembles the well-known Coulomb potential, while, on the crystal side, it converges to the inner potential. In theoretical calculations, the transition region is usually described by a parameterized phenomenological model. Our experiment provides access to exactly this transition region.

We could determine the spin-dependent shape of the surface-potential barrier of Co/Cu(001) from the dispersion of the fine structure as a function of polar and azimuth angle.

[1] T. Okuda *et al.*, Rev. Sci. Instrum. **79** (2008) 123117 ; [2] A. Winkelmann *et al.*, Rev. Sci. Instrum. **79** (2008) 083303 ; [3] R.O. Jones, P.J. Jennings, Surf. Sci. Reports **9**, 165 (1988)

# Tuesday Afternoon Poster Sessions

## Applied Surface Science Division

Room: East Exhibit Hall - Session AS-TuP

### Applied Surface Science Poster Session

**AS-TuP2 An Electrostatic Analytical Microscope for SEM/SAM Surface Studies with 3nm-7nm Spatial Resolution, A.R. Walker, M. Rignall,** Shimadzu Research Laboratory (Europe) Ltd., UK

A very high spatial resolution all electrostatic, ultra high vacuum, electron optical column has been developed for fast Nano analysis of specimen surfaces. The electron optical column does not project any electric or magnetic fields to the analysis region or beyond.

The electrostatic column operates with a beam energy range of 1-10keV, at a specified working distance of 10mm, for all survey and analytical modes of operation. Spatial resolutions of 4-7nm for Auger Nano analysis and 3nm for a SEM mode correspond to probe currents that range from 1nA to 0.25nA. Other modes of operation are available and these include operation at intermediate spatial resolutions <100nm with high probe currents of 100's nA and a very useful wide survey mode of ~5mm field of view at lower spatial resolutions <1 $\mu$ m. The electron optical column, having no magnetic lens components and therefore no hysteresis effects, is able to switch fast between these different modes.

Key to the electron optical column specification is the design of the probe forming electrostatic objective lens which operates in an accelerating mode. This lens design is a compact truncated cone with 80° apex angle at the analysis position (10mm WD) which enables a wide angular access (50°) to the specimen surface. Its electron optical design is an Einzel lens of asymmetrical electrode structure and operates with a positive potential of up to 50kV applied to its central electrode. The lens operation is extremely stable with no detectable electrical instabilities.

To aid the development of the electrostatic lens we use simulation software to calculate the lens parameters. At the objective lens WD of 10mm and object at infinity, low values of spherical aberration (75mm) and chromatic aberration (19mm) were computed. These values are comparable to the best magnetic lenses of similar external dimensions and working distance.

The column is mounted on a small analytical chamber for test purposes. We have demonstrated a 3nm SEM spatial resolution at beam energies of 10keV with 250pA of current. At a beam energy of 3keV with 150pA of current, we achieved and 7nm SEM spatial resolution.

An Auger signal was detected using a new form of hyperbolic field parallel energy analyser. A Gold Au (64eV) line scan demonstrated an edge resolution of 4.1nm using a primary probe of 10keV energy and 400pA of current.

For conventional energy analyzers, a probe current of 1nA is more appropriate and the spatial resolutions have been measured as 5nm and 7nm for respective beam energies of 10keV and 7keV.

**AS-TuP3 Core Level Shift from Experiment and First-Principles-Theory – A Comparison, B. Kiefer,** New Mexico State University, B. Halevi, K. Artyushkova, University of New Mexico

The knowledge of geometries and chemistry of functional motifs that causes particular materials behavior is crucial for the rational development of novel materials and materials based technologies. X-ray photoelectron spectroscopy (XPS) measures the binding energy (BE) changes that are induced on an atom by its surrounding ligands and by comparing to them to databases. However, in many cases the reference materials available in the databases are limited to common/model compounds, while actual materials designed may have more complicated chemistries. Furthermore, the big spread in the reported values of BE due to various ways to charge calibrate spectra and also sensitivity of BE to secondary environments present a big problem for accurate identification of unknown peaks in spectra.

Being able to calculate binding energy shifts based on molecular structure can be very important tool for identifying structural motifs in materials. There are only a few studies reporting density-functional-theory (DFT) calculations of BE energies due to challenges that are associated with the treatment of core electrons. Their high kinetic energy can require to include relativistic effects especially for heavy elements and absolute values of binding energies cannot be expected to be accurate. Furthermore the differences in reference state complicate the direct comparison between experiment and theory.

A possible solution to these challenges is to compare BE to a reference system that is accessible both in experiment and theory. We will report on BE shift that have been calculated and compared to experimentally obtained values for metallic, bimetallic and covalent systems. For metallic Pd (111) system, surface layers have lower binding energy, while sub-surface is bulk like. For bimetallic PdZn system, Pd(3d) and Zn(2p) shift upward with respect to fcc-Pd(3d) and for hcp-Zn(2p), respectively. Magnitudes of shifts are very similar to that obtained experimentally. For covalent system, such as metal-less and metal-containing porphyrins, shift for N 1s BE in Co 2p environment compared to N 1s without metal is also very close to that obtained experimentally.

**AS-TuP4 Evaluation of C<sub>60</sub> Depth Profiling Conditions for XPS Organic Films Analysis, S. Alnabulsi, S.R. Bryan, J. Moulder,** Physical Electronics

Type-II organic materials can be successfully depth profiled by XPS using C<sub>60</sub> ion beam sputtering at room temperature. Success is defined by achieving steady state composition as a function of depth. However, depth profiling of Type-I polymers have been marginally successful due to rapid sample damage under C<sub>60</sub> bombardment. The use of high C<sub>60</sub> beam energy at a glancing angle has been shown to extend the maximum depth of successful depth profiling, yet it eventually fails due to sample roughening, concomitant carbon build up, and a strong reduction in sputter rate.

Zalar (azimuthal) rotation has been shown to minimize sputter induced roughness formation, improve depth resolution in multi-layer film structures, and allow depth profiles to be extended to even greater depths. Cooling of the sample to below its glass transition temperature is expected to reduce the mobility and reactivity of free radicals that are formed during the sputtering process.

The purpose of this study is to evaluate the relative importance of using Zalar rotation and sample cooling to characterize standard organic thin film structures and to quantify the benefit to using them simultaneously.

**AS-TuP5 Development and Application of Novel Electron Energy Analyzers for Chemical Analysis of Surfaces, D. Cubric,** Shimadzu Research Laboratory (Europe) Ltd., UK, N. Kholine, Institute for Analytical Instrumentation, RAS, Russian Federation

Various instruments have been developed previously for analyzing the spectrum of energies of beams of charged particles emanating from surfaces and described in numerous publications [1]. Among all those instruments the concentric hemispherical analyser (CHA) and the cylindrical mirror analysers (CMA) have been the most often used instruments both commercially and for various devices developed by different laboratories. At first sight, geometry of the two analyser types is very different. However, topologically their geometries are very similar. This paper presents a line of thought where geometries of both analysers are just particular examples of a more general geometry that in turn provides numerous analyser configurations, that we now call spheroid energy analysers (SEA), often having excellent electron optical characteristics [2]. The SEA instrumental concept enables electron optical exploration of various new analyser embodiments, particularly well suited for chemical analysis of surfaces and surface nano-features. Progress in this instrumentation development and example spectra will be presented. **References** [1] D. Roy and D. Tremblay, Design of electron spectrometers, Rep. Prog. Phys. 53 (1990) 1621-1674 [2] D. Cubric, N. Kholine and I. Konishi, doi:10.1016/j.nima.2010.12.146

**AS-TuP6 Extreme Brightness: Reaching the Ultimate Limits of the Electron Beam, J.D. Jarvis, J.L. Kohler, B. Ivanov, N. De Jonge, B.K. Choi, A.B. Hmelo, C.A. Brau,** Vanderbilt University

We report recent results from field emission microscopy studies of multiwall carbon nanotubes (MWCNT) and from energy spectrum measurements of beams from diamond field emitters (DFE). As expected, resonant tunneling through adsorbed species on the emitter surface is an important and sometimes dominant effect. For diamond emitters our observations include order-of-magnitude emission enhancement without spectral broadening, complex spectral structure, and sensitivity of that structure to the applied electric field. For carbon nanotubes we have observed electron beams from individual adsorbates which are estimated to approach the maximum beam brightness allowed by Pauli exclusion.

The development of CNTs as field emitters for the purposes of microscopy, lithography, radiation generation, and display production has been a protracted endeavor. Working in their favor, CNTs have excellent emission stability, high activation energy for thermal migration, excellent current throughput capacity, and a high degree of chemical inertness. Not

surprisingly, these properties extend to other covalent-carbon structures such as CVD diamond field emitters. DFEs have shown great promise as high-brightness electron-beam sources in recent years. One of the more exciting revelations regarding CNTs and DFEs has been the realization that resonant tunneling through adsorbed species can be exploited for the generation of multi-microamp-level beams with perfect transverse coherence.

For resonant tunneling through a single molecule the electron source size is on the order of the electron wavelength. Estimates of the transverse momentum spread of the resulting electron beams suggest that the transverse emittance is Heisenberg limited. Such beams have been produced using single atom tungsten, or single atom noble-metal field emitters, however the relatively weak binding of the metal atoms has limited the total current that can be extracted to the sub-microamp regime. In this paper we will discuss our efforts to generate, stabilize, and characterize, multi-microamp beams from individual molecules on CNTs

**AS-TuP8 Surface Characterization of Disposable Laboratory Gloves by X-ray Photoelectron Spectroscopy (XPS),** *B.R. Strohmeier, C. Baily, T.S. Nunney*, Thermo Fisher Scientific, UK, *A. Plasencia*, Thermo Fisher Scientific, *J.D. Piasecki*, RJ Lee Group, Inc.

Disposable elastic gloves are ubiquitous in scientific laboratories and are also widely used in many industries during handling of critical surfaces. Disposable gloves are typically made from nitrile, latex, neoprene, or other polymers and offer their users protection from various aqueous acids and bases, biological fluids, organic solvents, and other potentially harmful chemicals. A second major application of disposable gloves is to protect manufactured products and analytical samples from contamination caused by the transfer of skin cells, oils, salts, or other residues resulting from contact with bare hands. However, disposable gloves can also be a potential source of contamination. In addition to the primary polymer structure, many types of common laboratory gloves also contain a variety of inorganic materials in the glove formulation. Mold-release agents that allow the gloves to be easily stripped from the glove formers during fabrication may be present on glove surfaces. Furthermore, many types of disposable gloves have polymeric surface coatings that provide improved donning properties. Contamination resulting from surface residues on gloves can adversely affect materials used in industries where surface cleanliness is essential for optimum product performance and can also interfere with the analysis of samples depending on the specificity and sensitivity of the analytical technique. X-ray photoelectron spectroscopy (XPS) is a qualitative and quantitative surface sensitive technique that can be used to evaluate the surface composition of disposable gloves and to determine if contamination transfer occurs from gloves in a specific process. In this study, XPS was used to characterize the surface compositions of a variety of common laboratory gloves. The transfer of surface components from gloves to other material surfaces and changes in the surface composition of gloves following exposure to several common laboratory solvents were also investigated.

**AS-TuP10 Large Area Cross Sectional Microstructural Characterization of ToF-SIMS Depth Profile Crater Walls,** *V.S. Smentkowski, D. Ellis*, GE-GR

Focused Ion Beam (FIB) techniques are widely used in order to generate cross sections of samples which can then be analyzed using a variety of analytical instrumentation in order to obtain microstructural information. In order to rapidly generate FIB cross sections, small areas (typically 5 to 10 microns) are milled. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful surface analytical technique that is able to measure low concentrations of sub surface species. ToF-SIMS depth profile measurements are collected by eroding a large area (50 to 1,000 microns in size) of a sample using an ion beam for a certain amount of time, pausing the erosion, analyzing a smaller (central) region of the eroded area, and repeating the cycle until the desired depth has been reached. Ion images are often recorded at each depth and a full mass spectrum is saved at every volume element allowing for 3 D analysis. Often times, both ToF-SIMS depth profile analysis and high resolution microstructural SEM characterization are required on the same sample. Ideally, these complimentary analyses would be performed in the same region of a sample. In this presentation, we will demonstrate that FIB techniques can be used to clean up the large area craters produced by ToF-SIMS depth profile analysis thereby enabling microstructural characterization over larger areas of samples.

Advantages of this approach are: larger FIB cross sections can be prepared since a significant amount of material was removed during the erosion cycles in the ToF-SIMS analysis, combining the chemical information provided from the ToF-SIMS analysis with the large area microstructural characterization provided by FIB-SEM analysis, and having both the ToF-SIMS and the large area cross sectional analysis performed in the same region of the sample. The ToF-SIMS depth profile craters have a slope of

about 45 deg (the ion column is positioned at an angle of 45 deg from the sample normal), and hence an advantage of performing the FIB clean up at this angle is the enhancement in the layer thickness that will be available for microstructural analysis.

**AS-TuP11 Microphase Separation of Various Diblock Copolymers Investigated by TOF-SIMS Depth Profiling,** *Y. Lee*, Korea Institute of Science and Technology, Republic of Korea, *J. Lee*, Korea University, *W.C. Lim*, Korea Institute of Science and Technology, *K. Shin*, Sogang University, Korea, *K.-J. Kim*, Korea University

Diblock copolymers, composed of two distinct homopolymers covalently bonded together at one end, exhibit a microphase separation from a disordered state to an ordered state on cooling or heating. The microphase separation of diblock copolymers has been investigated by many different research groups for many years, because of the increasing use of diblock copolymers as compatibilizers, dispersants, impact modifiers, nanocarriers, and templates. Investigation of the phase behaviour of a family of diblock copolymers between styrene and a homologous series of methacrylates or acrylates has revealed that significantly different phase behaviours are seen for these materials, depending on the temperature, molecular weight, and alkyl side chain length. In this work, we characterized the morphology from various diblock copolymers of poly(styrene-*b*-alkyl acrylate)(PS-PAA), where PS block was perdeuterated, near the copolymer/air and copolymer/substrate interfaces and in the bulk using time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS). ToF-SIMS Depth Profiling was obtained for the lamellar morphology of PdS-PAA which is found to orient parallel to the surface of the substrate. This preferential orientation resulted in a periodic variation in the composition of each block that continued through the entire copolymer film. Temperature- and chain length-dependent annealing studies on PdS-PAA thin films on the silicon substrates were performed to investigate the order-to-disorder transition (ODT) properties of diblock copolymers.

**AS-TuP12 Analysis of Passivated Surfaces for Mass Spectrometer Inlet Systems by Auger Electron and X-Ray Photoelectron Spectroscopy,** *H.M. Ajo, D.W. Blankenship, E.A. Clark*, Savannah River National Laboratory

Stainless steel coupons approximately 0.5" in diameter and 0.125" thick were passivated with five different surface treatments and an untreated coupon was left as a control. These surface treatments are being explored for use in tritium storage containers. These coupons were made to allow surface analysis of the surface treatments using well-known surface analysis techniques. Depth profiles using Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were performed on these coupons to characterize the surface and near surface regions. Scanning electron microscope (SEM) images were collected as well. All of the surface treatments studied here appear to change the surface morphology dramatically, as evidenced by lack of tool marks on the treated samples. In terms of the passivation treatment, Vendors A-D appeared to have oxide layers that were very similar in thickness to each other (0.7-0.9 nm thick) as well as the untreated samples (the untreated sample oxide layers appeared to be somewhat larger). Vendor E's silicon coating appears to be on the order of 200 nm thick.

**AS-TuP13 Surface Characterization of Gunshot Residue (GSR) by X-ray Photoelectron Spectroscopy (XPS) and High Resolution Electron Microscopy,** *A.J. Schwoeble*, RJ Lee Group, Inc., *B.R. Strohmeier*, Thermo Fisher Scientific, *K.L. Bunker, D.R. McAllister, J.P. Marquis, Jr., J.D. Piasecki, N.M. McAllister*, RJ Lee Group, Inc., *W. Sgammato*, Thermo Fisher Scientific

Discharged firearm cartridges produce unique microscopic particles referred to as gunshot residue (GSR). GSR is primarily composed of the products of combustion of the cartridge primer materials and typically contains varying amounts of Pb, Sb, and Ba, plus other elements. GSR particles can range in size from tens of nanometers to hundreds of micrometers. 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. Computer-controlled scanning electron microscopy (CCSEM) is the method preferred by the forensic community for the automated analysis of GSR. With CCSEM, large populations of potential GSR particles in the size range of ~1-10 µm are rapidly screened for the characteristic presence of combinations of Pb, Sb, and Ba using energy dispersive X-ray spectroscopy (EDS). Determining the presence of these three elements fused together in a single particle having the correct morphology is all that is normally required for the positive identification of GSR. CCSEM, however, does generally not provide information regarding the population of particles much less than 1 µm. In addition, little is presently known regarding the surface chemistry of GSR. 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. This work examines the fine fraction of GSR particles with high resolution electron microscopy methods and complements the microscopy data with surface chemistry information obtained from XPS.

**AS-TuP14 Analysis of Graphene and Other Graphitic Materials using XPS and AES, H.M. Meyer III, Oak Ridge National Laboratory**

Synthesis and characterization of advanced carbon materials, including graphene, has accelerated over the past several years at the Oak Ridge National Laboratory. Projects include, among others, the development of nanostructured carbon materials for batteries, fuel cells and as supports for revolutionary catalysts. The past year has also brought to ORNL new projects related to the growth, characterization and application of graphene. This poster will highlight x-ray photoelectron spectroscopy and scanning Auger microanalysis of a variety of important carbon materials from several of these research projects, including nano-sized carbon powders for battery applications, graphitic carbon powders used in fuel cells, graphene flakes synthesized for supporting catalyst materials and CVD grown graphene. In particular, an approach for curve fitting highly graphitic materials will demonstrate internally consistent results, giving insight into the  $sp^2$  vs.  $sp^3$  type carbon atoms present in the material.

Research sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

**AS-TuP15 Investigation of Precious-Metal/Metal-Oxide-Support Interactions in Automotive Catalytic Converters using a Pd/Ce<sub>0.7</sub>Zr<sub>0.3</sub>O<sub>2</sub> Model Planar Catalyst System, O.K. Ezekoye, University of Michigan, M.I. Nandasiri, Western Michigan University, T. Varga, P. Nachimuthu, W. Jiang, S.V.N.T. Kuchibhatla, S. Thevuthasan, Pacific Northwest National Laboratory, X. Pan, G.W. Graham, University of Michigan**

Ceria-zirconia mixed oxide (CZO) has been incorporated into automotive catalysts as a support material for precious metals (Pt, Rh, Pd) due to its highly desirable redox properties. However, at high operating temperatures, certain interactions between CZO and precious metal particles may adversely affect the performance of the catalytic converter. Thus, it is important to investigate the CZO/precious-metal interactions under redox conditions. Here, the preparation of Pd/CZO thin films as model planar catalyst systems will be described together with a systematic study of an important adverse interaction, the encapsulation of Pd particles by CZO, using a combination of x-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM).

Ceria-zirconia ( $Ce_{0.7}Zr_{0.3}O_2$ ) thin films with thickness ranging from 10-200 nm were grown on (111) yttria-stabilized zirconia (YSZ) by oxygen plasma assisted molecular beam epitaxy (OPA-MBE). The epitaxial layer growth of CZO on YSZ(111) was confirmed by in-situ reflection high energy electron diffraction (RHEED). Atomic force microscopy (AFM) images revealed the smooth surface of the films with low roughness values (3-8 Å). Rutherford backscattering spectrometry (RBS) data along channeling and random geometries showed the minimum yield ( $\chi_{min}$ ) of 13% for Ce with no inter-diffusion of metal atoms at the film/substrate interface. The single crystal nature of the film with CZO(111) orientation was confirmed by XRD data. Following the growth and characterization of thin films, ~1 monolayer of Pd was deposited on CZO(111) by thermal evaporation in a UHV chamber. After air calcination at 600 °C, the Pd/CZO films were reduced in 1%  $H_2/N_2$  at 200°C, followed by annealing in  $N_2$  at 700 °C. Due to the additional reduction-induced compressive stress, the 10 nm and 40 nm films broke up and formed a rough surface with 10-20 nm CZO mesas, as observed by HRTEM. However, films with a thickness above ~50 nm were stable, and Pd particles that formed on the surface became partially encapsulated by migration of CZO. In the films with a thickness above ~50 nm, the native compressive stress induced by the lattice mismatch between the film and substrate was relaxed by misfit dislocations at the interface, as revealed by high resolution scanning TEM images, to varying degree, depending on film thickness, but the extent of encapsulation appeared to be about the same for all film thicknesses. These results suggest that the driving force for the partial encapsulation resides in the nature of CZO, and is not simply a consequence of the lattice-mismatch-induced compressive stress in the films.

**AS-TuP17 Cleaning and Characterization of InP Surface using Atomic Hydrogen and STM, W. Melitz, J. Shen, T. Kent, University of California San Diego, R. Droopad, Texas State University, P.K. Hurley, Tyndall National Institute, A.C. Kummel, University of California San Diego**

Metal oxide semiconductor field effect transistors (MOSFETs) are the dominant logic device in modern electronics. Due to the challenges of scaling Si-MOSFETs alternative materials are being explored to improve device performance. III-V semiconductors are of interest for use in MOSFETs due to their high mobilities, but in order to make these devices competitive the semiconductor-oxide interface needs to have a low density of interfacial traps ( $D_{it}$ ) in order to minimize subthreshold swings and also be atomically flat to allow high mobility at high field strengths. Current Si-MOSFET fabrication uses a gate last process which is an attractive method because it minimizes the gate oxides exposure to harsh processing conditions. In order for gate last processing to provide a nearly defect free semiconductor-oxide interface for surface channel devices, the channel surface must be in pristine condition before the oxide layer is deposited. In addition the oxide deposition process cannot introduce any defects. Recent advances show that a thin indium phosphide layer deposited on top of the InGaAs channel may provide superior electronic performance because the InGaAs/InP interface is defect-free and flat while the defects at the oxide/InP interface are less detrimental to device performance than the defects at the oxide/InGaAs interface.

In order to facilitate gate last processing of the InP/InGaAs channel stack, a four step process was investigated to clean and nucleate atomic layer deposition (ALD) of an InP/InGaAs surface. Samples were grown with an undoped 2 nm InP layer on ~1  $\mu m$  InGaAs layer doped with  $4 \times 10^{18} cm^{-3}$  of Si on an InP wafer. Using in-situ atomic imaging (scanning tunneling microscopy), electronic measurements (scanning tunneling spectroscopy), and XPS a four step in-situ process was developed for converting an air-exposed InGaAs(100)-4x2 surface into a flat, electronically passivated, mono-layer nucleation template for ALD of gate oxides. The optimized process includes a small dose of atomic hydrogen, annealing to reduce surface roughness, TMA dosing to functionalize the surface, and a final annealing to induce a highly ordered ALD nucleation layer. Following atomic hydrogen cleaning at 380°C and annealing at 470°C, the surface was exposed to  $\sim 1 \times 10^{-2}$  Torr of TMA at room temperature and annealed to 270°C. The TMA induces a surface reconstruction consistent with a bulk like bonding configuration between the Al atoms and the surface P atoms. The TMA passivation layer has horizontal rows of DMA. The cleaning and nucleation process does not disrupt the InP surface thereby providing a path for further scaling of the InP layer and the gate oxide.

**AS-TuP18 Highly Selective and Low Damage Etching of GaAs/AlGaAs Heterostructure using Cl<sub>2</sub>/O<sub>2</sub> Neutral Beam, J.S. Oh, K.S. Min, C.K. Kim, G.Y. Yeom, Sungkyunkwan University, Korea**

Highly selective and low damage etching of the GaAs cap layer on AlGaAs is essential in fabricating devices such as heterojunction superlattices, field effect transistors, injection lasers, and solar cells, etc. The GaAs on AlGaAs was etched using a low energy  $Cl_2/O_2$  neutral beam and the schottky device characteristics fabricated on the exposed AlGaAs were compared with those fabricated after the etching using wet etching and a  $Cl_2/O_2$  ion beam. The wet etching was conducted by a mixture of  $H_2O_2$  and  $H_3PO_4$ . For the  $Cl_2/O_2$  neutral beam etching, a neutral beam system composed of three-grid inductively coupled plasma (ICP)-type ion gun and a reflector installed just in front of the ion gun was used. Using a low energy  $Cl_2/O_2$  ion beam or a  $Cl_2/O_2$  neutral beam, highly selective etching of the GaAs cap layer to AlGaAs similar to wet etching could be achieved through the formation of  $Al_2O_3$  on the exposed AlGaAs during the etching. When the electrical characteristics of the schottky devices were compared, the devices fabricated after the etching using the neutral beam showed the best electrical characteristics such as electrical stability, low leakage current, higher barrier height, etc. by showing low damage to the exposed AlGaAs surface.

**AS-TuP19 TiO<sub>2</sub> Nanotube Growth Mechanism Studied with Scanning Auger Spectroscopy, D.F. Paul, Physical Electronics, S. Berger, F. Schmidt-Stein, S.P. Albu, H. Hildebrand, P. Schmuki, University of Erlangen-Nürnberg, Germany, J.S. Hammond, Physical Electronics**

Anodic  $TiO_2$  nanotubes offer unique properties for a wide range of applications including energy conversion, photocatalysis and biomedical devices<sup>1,2,3</sup>. It is widely accepted that the initial growth of the nanotubes is based on the formation of a compact anodic oxide followed by the formation of etching grooves and pores in the oxide<sup>4,5</sup>. The mechanism of steady state growth of the nanotubes from the embryonic pores has, however, remained a topic of debate. To evaluate a flow model<sup>1,6</sup> for the formation of the tubular structures, high spatial resolution Scanning Auger Spectroscopy data is used to elucidate the compositional variations across  $TiO_2$  nanotube layers grown in a fluoride containing ethylene glycol electrolyte. The layers were fractured parallel to the axes of the nanotubes

and quantitative spectra, line scans and elemental maps were acquired along the walls of the nanotubes. The Auger data indicates the presence of a fluoride rich layer located between the tube walls, and in particular, the triple points of the hexagonally ordered nanotube arrays. This data supports fluoride dissolution as the reason for a transition from a porous oxide layer to tubular structures. This data also supports a flow model as a mechanism for the formation of the tubular morphology.

**AS-TuP20 Effect of Annealing TiN/Al<sub>2</sub>O<sub>3</sub> Nanofilms Grown on InGaAs.** O. Ceballos-Sanchez, A. Sanchez-Martinez, M.O. Vazquez-Lepe, CINVESTAV-Unidad Queretaro, Mexico, P. Lysaght, SEMATECH, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, Mexico

III-V compounds are candidates to replace Si as the semiconductor in complementary metal-oxide-semiconductor (CMOS) devices.<sup>1</sup> The extensive research for over 40 years in the field of III-V semiconductors reflects the efforts that have been made to find new materials that meet the technological needs. InGaAs is one of the most promising compounds because of its high electron mobility and flexible bandgap as compared to Si.<sup>2</sup> However, one difficulty associated to III-V semiconductors is the lack of high-quality and thermodynamically stable gate dielectric insulators that passivate the interface. Growing Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub> and ZrO<sub>2</sub> by atomic layer deposition (ALD) on InGaAs or III-V semiconductors have shown the removal of native oxide and the passivation of the high-*k*/III-V interface.<sup>3</sup> However, the high temperatures (~850°C) required for the activation of some dopant in the device induce structural changes that degrade the properties of the interface.<sup>4</sup> The appearance of oxides, defects or even the diffusion of atoms within the material are issues that primarily affects the device performance. The poor ultimate resolution achieved with some of the characterization techniques traditionally employed for the assessment of the chemical depth profile of thin films limits the quantitative analysis of the structure and composition of the films. In this work we present an analysis by angle-resolved x-ray photoelectron spectroscopy (ARXPS) of TiN/Al<sub>2</sub>O<sub>3</sub>/In<sub>x</sub>Ga<sub>1-x</sub>As nanofilms with different thermal treatments (no-annealing, 500 °C for 2 min, and 700 °C for 10 s). The purpose of the study was to investigate possible reasons of the interface degradation. Through a self-consistent approach based on a multilayer model (MLM), a quantitative study was performed for the composition and thickness of the TiN/Al<sub>2</sub>O<sub>3</sub>/InGaAs nanofilms. The results clearly show that indium diffuses towards the metal layer as a consequence of heat treatments, suggesting a possible failure mechanism. [1] Han Zhao, Jeff Huang, Yen-Ting Chen, Jung Hwan Yum, Yanzhen Wang, Fei Zhou, Fei Xue, and Jack C. Lee, Appl. Phys. Lett. **95**, 253501 (2009). [2] F. S. Aguirre-Tostado, M. Milojevic, C. L. Hinkle, E. M. Vogel, R. M. Wallace, S. McDonnell, and G. J. Hughes, Appl. Phys. Lett. **92**, 171906 (2008). [3] Y. Xuan, H.C. Lin, and P.D. Ye, Appl. Phys. Lett. **88**, 263518 (2006). [4] Y. Xuan, P.D. Ye, and H.C. Lin, Appl. Phys. Lett. **89**, 132103 (2006).

**AS-TuP21 Comparison between the Continuous and Discrete Model to Assess the Thickness of SiO<sub>2</sub> Layers on Si with XPS Data.** M.O. Vazquez-Lepe, P.G. Mani-Gonzalez, A. Mendoza-Galvan, A. Herrera-Gomez, Cinvestav Queretaro Mexico

X-ray Photoelectron Spectroscopy (XPS) is a valuable tool for assessing the thickness of surface layers in the 0 to 8 nm range. The prediction of a core-level XPS signal from a solid requires assuming a specific volumetric distribution of such core levels. Since the core levels are spaced close to the atomic nucleus, a possible approximation is to model their volumetric distribution as a sum of delta functions at the atomic sites. Another approach is to consider that the source of the photoelectrons is uniformly distributed within the volume of the solid. The latter is called the *continuous approximation* (CA) and the former the *discrete approximation* (DA). The CA is widely employed; it leads to an expression for the XPS signal proportional to  $c\lambda \sin \alpha$ , where  $c$  is the volumetric density,  $\lambda$  is the effective attenuation length, and  $\alpha$  is the take off angle. The DA applied to crystalline structures leads to an expression proportional to  $s[1 - \exp(-a/(\lambda \sin \alpha))]^{-1} \exp(-a/(2\lambda \sin \alpha))$ , where  $a$  is the spacing of the atomic planes parallel to the surface, and  $s$  is the atomic plane surface concentration ( $s/a = c$ ) [1]. When  $a/\lambda \ll 1$ , the DA expression reduces to the corresponding to CA. Applying the DA to amorphous materials requires defining an "effective" or "average" atomic spacing ( $a_e$ ) and surface concentration ( $s_e$ ). In this paper we compare the differences on the thickness of silica layers on Si[001] calculated with these two approaches. The analysis was done by employing XPS data at one angle or at various angles (ARXPS). The samples employed were thermally grown silica at 800 °C for 16 s, 75 s, 145 s, 212 s and 7 min. The results are also compared to more standard methods [2], such as that employing the parameter  $R$  (ratio of the Si 2p XPS intensities for clean Si and thick SiO<sub>2</sub>). The thickness of the silica layers were also assessed from Transmission Electron Microscopy (TEM) images and correlated to Ellipsometry measurements. It was found that the approach employing the DA and various angles better reproduced the TEM measurements.

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**AS-TuP22 Electrical and Surface Studies of the High-*k* Gate Dielectrics Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and Al<sub>x</sub>Hf<sub>1-x</sub>O<sub>2</sub> on Silicon via Atomic Layer Deposition.** S. Hogan, G. Hernandez, R. Candler, S. Franz, Y.S. Lin, UCLA

As the demand for high speed electronics remains ever increasing, the dimensions of MOSFET technology are continuously scaled down to the smallest possible levels. Traditional gate dielectrics such as SiO<sub>2</sub> are unable to effectively stop electron tunneling from degrading device performance at thicknesses below 1-1.2 nm. We propose using high dielectric materials instead, which can effectively limit leakage current and have a band gap close to SiO<sub>2</sub>. This study will focus on the dielectrics Al<sub>2</sub>O<sub>3</sub>, HfO<sub>2</sub>, and Al<sub>x</sub>Hf<sub>1-x</sub>O<sub>2</sub> deposited using ALD. Several ratios of aluminum and hafnium in the Al<sub>x</sub>Hf<sub>1-x</sub>O<sub>2</sub> compound will be investigated to find a level that maximizes both electrical and physical properties of the film. The electrical properties of each dielectric will be characterized by XPS, AFM, spectroscopic ellipsometry, and by taking IV and CV measurements of fabricated transistors and capacitors. We will also investigate the effects of different annealing and deposition temperatures on the interface by TEM.

**AS-TuP23 Enhanced Green Emission from UV Down-Converting Ce<sup>3+</sup>-Tb<sup>3+</sup> Co-Activated ZnAl<sub>2</sub>O<sub>4</sub> Phosphor.** K.G. Tshabalala, University of the Free State, South Africa, S. Cho, J. Park, Korea Institute of Science and Technology, Republic of Korea, H.C. Swart, O.M. Ntwaeaborwa, University of the Free State, South Africa

Ce<sup>3+</sup>-Tb<sup>3+</sup> co-activated ZnAl<sub>2</sub>O<sub>4</sub> nanocrystal phosphors were prepared by a solution combustion method using urea (CH<sub>4</sub>N<sub>2</sub>O, 99.0–99.5%) as a fuel. The samples were annealed at 700°C for 4 hrs, in a tubular furnace, in a reducing atmosphere containing a mixture of 4% H<sub>2</sub> and 96% N<sub>2</sub>. The X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) data showed that a well known cubic normal spinel structure of ZnAl<sub>2</sub>O<sub>4</sub> was crystallized. In addition, the HRTEM data showed that the particles were spherical with some degree of faceting. Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were used respectively to analyze the chemical composition of the phosphors and electronic states of individual elements. The XPS data demonstrated that there was structural readjustment of ZnAl<sub>2</sub>O<sub>4</sub> from normal to spinel inversion due to annealing. An enhanced down-converted green emission associated with the <sup>3</sup>D<sub>4</sub>→<sup>7</sup>F<sub>5</sub> transitions of Tb<sup>3+</sup> was observed at 543 nm from the ZnAl<sub>2</sub>O<sub>4</sub>:Ce<sup>3+</sup>, Tb<sup>3+</sup> powders with different concentrations of Ce<sup>3+</sup> and Tb<sup>3+</sup>. It was confirmed from the fluorescence decay data that the enhancement was due to energy transfer from Ce<sup>3+</sup> to Tb<sup>3+</sup> ions. Possible mechanism of UV down-conversion will be discussed. In addition, cathodoluminescence (CL) intensity degradation was evaluated for possible application of this material as a green emitting phosphor in field emission displays.

**AS-TuP24 Characterization of Al<sub>x</sub>Ga<sub>1-x</sub>N Thin Film Light Emitting Diode (LED) Device by Spectroscopic Ellipsometry.** K. Uppireddi, L. Yan, HORIBA Scientific

The demand for efficient energy usage for lighting at industry viable production costs catalyzing the rapid growth of global LED market. LED lighting is widely in use from LED-backlit TVs to solid-state lighting. The wall-plug efficiency, which characterizes its performance depends on the design and material properties of thin film LED structure. The accurate determination of thickness and composition of the well and barrier layers is desired for quality control in the production. The Sapphire/AlN/Al<sub>x</sub>Ga<sub>1-x</sub>N structure was characterized using a phase modulated spectroscopic ellipsometer (PMSE) at an angle of incidence of 70 degree across the spectral range 0.6-6.5 eV. Using a three layer structure we accurately modeled the thickness of the layers in the spectral range from 0.6 to 4.5 eV and Al<sub>x</sub>Ga<sub>1-x</sub>N optical constants. The PMSE delivers both unique performance and proven reliability for on-line quality control of production process.

**In Situ Spectroscopy and Microscopy Focus Topic  
Room: East Exhibit Hall - Session IS-TuP**

**In Situ Spectroscopy and Microscopy Focus Topic Poster  
Session**

**IS-TuP1 In Situ Infrared Spectroscopy of Oxidation Process of Amorphous Carbon Film, Depending on Substrate Temperatures, M. Shinohara, Y. Takaki, K. Hara, Y. Takami, Y. Matsuda, H. Fujiyama, Nagasaki University, Japan**

There has been much interest in amorphous carbon films because they have a lot of useful properties: mechanical hardness, chemical inertness, and changeable electrical properties. The films can be deposited at low temperatures by using plasma process. The films have been used as coating materials for mechanical apparatus. The property of the film surface can be change with the addition of the other atoms on the surface. The addition of oxygen atoms to the surface leads the surface hydrophilic. The hydrophilic property on the surface has advantages to the further surface treatment. Therefore, it is important to understand the oxidation process of amorphous films. One of the effective oxidation methods is oxygen plasma exposure. We investigated the plasma oxidation process with in-situ infrared spectroscopy in multiple internal reflection geometry (MIR-IRAS). In this presentation, we focus on the dependence of oxidation process on the substrate temperatures. Infrared spectroscopic studies indicated that the oxygen plasma exposure induced the generation of OH components in the film. It means that carboxyl group would be formed by the exposure. With the increases of the substrate temperatures, the formation of OH components in the film was suppressed; moreover, the hydrophilic property was decreased with the substrate temperatures. On the other hand, the etching rate due to the oxygen plasma exposure was increased with the substrate temperatures. It is suggested that the etching rate is increased with substrate temperature, compared with the preservation of the OH components in the film.

**IS-TuP3 In Situ TEM Studies of Nanoparticle Growth in a Fluorozirconate (ZBLAN) Glass Matrix, J. Johnson, University of Tennessee Space Institute**

ZBLAN glass-ceramic materials are being developed as x-ray imaging plates. The materials are doped with europium and chlorine and can be heat treated in such a way that they form a novel nanocomposite material containing barium chloride nanocrystals, with the ability to convert x-rays into stable electron-hole pairs. The image can be read out afterwards with a scanning laser beam in a photostimulated luminescence process.

The ZBLAN glass only acts as an imaging plate upon annealing. As the annealing temperature and annealing time are increased, so a higher degree of nucleation of BaCl<sub>2</sub> crystallites inside the glass matrix is observed. As a result, more crystallites are available to incorporate Eu<sup>2+</sup> and hence increase the fluorescence intensity. However, a higher annealing temperature and a longer annealing time also lead to a larger degree of crystal growth, resulting in bigger nanoparticles. This leads to a decrease in spatial resolution of a ceramic-glass storage phosphor. The optimal annealing condition thus needs to compromise between the fluorescence intensity and the spatial resolution.

Here we present *in situ* TEM studies of ZBLAN glasses, being carried out to further understand the growth of nanoparticles inside a glass matrix under various heating conditions.



# Wednesday Morning, November 2, 2011

## Applied Surface Science Division

Room: 102 - Session AS+BI+NS-WeM

### Advances in Scanning Probe Microscopy

Moderator: S.A. Allen, The University of Nottingham, UK

8:00am AS+BI+NS-WeM1 **High-Speed Atomic Force Microscopy for Filming Biomolecular Processes**, T. Ando, Kanazawa University, Japan

INVITED

Vital phenomena are engendered through the dynamic activity of biological molecules. Therefore, observing the dynamic behavior of biological molecules in action at high spatiotemporal resolution is essential for elucidating the mechanism underlying the biological phenomena. The dynamic biomolecular processes are now widely studied using single-molecule fluorescence microscopy. However, the fluorescently labeled biological molecules themselves are invisible in the observations even using super-resolution fluorescence microscopy. The structure of biological molecules has been studied using x-ray crystallography, NMR, electron microscopy, and atomic force microscopy (AFM) but the obtained structures are essentially static. Thus, the simultaneous assessment of structure and dynamics is infeasible. To overcome this long-standing problem and make it possible to simultaneously record the structure and dynamics of biological molecules, we have been developing high-speed AFM for more than 15 years and at last it is now coming of age. Various AFM devices and control techniques were optimized or invented for high-speed scanning and low-invasive imaging. As a result, the imaging rate now reaches 10-30 frames/s for the scan range  $250 \times 250 \text{ nm}^2$ , 100 scan lines, and the spatial frequency of a sample surface corrugation 0.1/nm [Prog. Surf. Sci. **83**, 337-437 (2008)]. Remarkably, even delicate protein-protein interactions are not disturbed by the tip-sample contact. With this capacity of high-speed AFM, some biological processes are successfully captured on video, such as walking myosin V molecules along actin filaments [Nature **468**, 72-76 (2010)], photo-activated structural changes in bacteriorhodopsin [Nat. Nanotechnol. **5**, 208-212 (2010)], and cooperative GroEL-GroES interactions. The high-resolution movies not only provide corroborative 'visual evidence' for previously speculated or demonstrated molecular behaviors but also reveal more detailed behaviors of the molecules, leading to a comprehensive understanding of how they operate. Thus, the high-speed AFM imaging of functioning biological molecules has the potential to transform the fields of structural biology and single-molecule biology.

8:40am AS+BI+NS-WeM3 **Integrated Imaging: Probing Molecular Interactions by Correlated Atomic Force Microscopy Approaches**, C. Yip, University of Toronto, Canada

INVITED

The development of powerful single molecule functional imaging tools has been critical to our understanding of molecular dynamics and structure-function relationships in (bio)molecular systems. Our lab's focus on the design, implementation, and application of coupled imaging and spectroscopy is providing intriguing insights into the mechanisms of membrane disruption, receptor oligomerization, and protein-membrane interactions. We have devised several correlative approaches based on the integration of in situ atomic force microscopy with fluorescence and vibrational spectroscopies for extracting the orientation, conformation, and association dynamics of membrane-associated proteins in model membranes and in live cells. Some of the key challenges and opportunities afforded these new tools will be discussed.

9:20am AS+BI+NS-WeM5 **Visible Light Emission from Fluorescent Proteins on Silver Substrate Induced by Tunneling Electrons**, T. Yamada, RIKEN, Japan, T. Iwaya, S. Matsunaga, M. Kawai, The University of Tokyo, Japan

We detected the characteristic visible light emission from fluorescent protein molecules deposited on metallic silver (Ag) upon injection of tunneling electrons generated by a standard scanning tunneling microscope (STM) in ambient condition. A series of fluorescent proteins originating from jellyfish or coral, nowadays engineered to generate various colors of fluorescence by gene technology, is characterized with a  $\beta$ -barrel structure insulating the chromophore electronically from the surrounding. We purchased green, yellow, red and infrared fluorescent proteins (GFP, YFP, RFP, HcRed, molecular diameter  $\approx 5 \text{ nm}$ ), deposited on a bare Ag surface, and used a Ag tip set on a STM setup to obtain images and to generate fluorescence. Light from the gap was collected by an optical fiber and introduced to a grating spectrometer with a liquid N<sub>2</sub>-cooled CCD detector. On bare Ag surfaces, visible light was detected with the STM bias voltage within  $\pm 1.8 \text{ V}$  in a modestly moisturized N<sub>2</sub> atmosphere. The spectra were

unstable in general, indicating light emission upon excitation of local plasmon [1], which depends on the changeable geometry of Ag tip. The wavelength onset of emitted light was equivalent to the STM bias voltage within  $\pm 3.0 \text{ V}$ , obeying the law of quantum energy conservation. The fluorescent proteins were dissolved in pure water, drop-cast on the Ag substrate and air-dried to form multilayers. STM images mostly showed flat terraces with steps composed of the protein molecules. Within a  $200 \text{ nm} \times 200 \text{ nm}$  scanning area, the light emission spectra apparently involved the characteristic fluorescence peaks of proteins (GFP = 540 nm (2.30 eV), YFP = 550 nm (2.25 eV), RFP = 650 nm (1.91 eV), HcRed = 660 nm (1.88 eV)) over a background of weakened Ag plasmon spectrum. The same experiment with Au tips and Au(111) substrates was with almost no detection for the characteristic fluorescence of all the proteins. For clean Au(111), although visible light was detected, the above-mentioned plasmon energy conservation stood for the bias voltage only within  $\pm 1.9 \text{ V}$ . The maximum energy of local plasmon on Au(111) is too small to excite the fluorescent proteins electronically. The characteristic fluorescence from proteins is considered aided by the plasmon excitation of the Ag substrate. The protein  $\beta$ -barrel structure reserves the lifetime of excited state towards light emission, insulating electronically from the metallic substrate against the radiationless de-excitation process of the present surface-adsorbate system.

References:

[1] F. Rossel, M. Pivetta, W.-D. Schneider, *Surf. Sci. Rep.* **65**, 129 (2010).

9:40am AS+BI+NS-WeM6 **Characterization of Peptide Nanotubes by Atomic Force Microscopy**, J.L. Remmert, M.C. Vasudev, Air Force Research Laboratory, L. Eliad, E. Gazit, Tel Aviv University, Israel, T.J. Bunning, R.R. Naik, A.A. Voevodin, Air Force Research Laboratory

This work investigates the properties of aromatic dipeptides, which are of interest due to their ability to self-assemble into nanotubes and nanowires. Peptide nanotubes have been used to template inorganic materials<sup>1</sup> and construct nanochannels in microfluidic devices<sup>2</sup>. The mechanical, thermal, and electronic transport properties of these nano-structures are desired to evaluate their potential use for biomolecular electronics<sup>3</sup> and other applications. Atomic Force Microscopy (AFM) offers multiple modes to interrogate the response of discrete nanotubes. For instance, AFM with dry sample heating has established the thermal stability of peptide nanotubes up to  $100 \text{ }^\circ\text{C}$ <sup>4</sup> with a spring constant of 160 N/m at room temperature<sup>5</sup>. A separate study targeting a single nanowire bridging two electrodes revealed semiconductor characteristics under repeated bias cycling<sup>6</sup>. We have similarly sampled detached nanotubes among peptide bundles and vertically aligned 3D arrays. Peptide nanotubes were synthesized by either Plasma Enhanced Chemical Vapor Deposition (PECVD) or solvent phase growth in 1, 1, 1, 3, 3, 3 Hexafluoroisopropanol (HFIP), using approaches similar to that described by Reches et al<sup>1</sup>. The nanotubes were observed by SEM to vary between 85-100 nm in diameter and up to 50  $\mu\text{m}$  in length. Sample density was controlled by suspension and dilution in various solvents, including HFIP and water, prior to deposition on a variety of substrates. AFM studies have revealed details of the tubular outer shell with tapping and electrostatic force modes (EFM), while also probing the mechanical integrity and thermal response to localized tip-side heating.

<sup>1</sup>M. Reches, E. Gazit, "Casting Metal Nanowires within Discrete Self-Assembled Peptide Nanotubes", *Science* **300** 625 (2003)

<sup>2</sup>N. Sopher, Z. Abrams, M. Reches, E. Gazit, Y. Hanein, "Integrating peptide nanotubes in micro-fabrication processes", *J Micromech Microeng* **17** 2360 (2007)

<sup>3</sup>V. Dinca, E. Kasotakis, J. Catherine, A. Mourka, A. Ranella, A. Ovsianikov, B. Chichkov, M. Farsari, A. Mitraki, C. Fotakis, "Directed Three-Dimensional Patterning of Self-Assembled Peptide Fibrils", *Nano Lett* **8** 538 (2008)

<sup>4</sup>V. Sedman, L. Adler-Abramovich, S. Allen, E. Gazit, S. Tendler, "Direct Observation of the Release of Phenylalanine from Diphenylalanine Nanotubes", *J Am Chem Soc* **128** 6903 (2006)

<sup>5</sup>N. Kol, L. Adler-Abramovich, D. Barlam, R. Shneck, E. Gazit, I. Rouso, "Self-Assembled Peptide Nanotubes Are Uniquely Rigid Bioinspired Supramolecular Structures", *Nano Lett* **5** 1343 (2005)

<sup>6</sup>J. Lee, I. Yoon, J. Kim, H. Ihee, B. Kim, C. Park, "Self-Assembly of Semiconducting Photoluminescent Peptide Nanowires in the Vapor Phase", *Angew Chem Int Edit* **50** 1164 (2011)

10:40am **AS+BI+NS-WeM9 Determination of Molecular Polarization at Protein-Electrode Interfaces with Combined Optical, Transport, and Dielectric Scanning Probe Microscopy.** *X. Chen, K. Kathan-Galipeau, B.M. Discher, D.A. Bonnell*, University of Pennsylvania

Bio-molecule integrated electronic devices are of great interest recently. For such systems to be designed and fabricated, the optoelectronic properties of protein molecules in ambient environment must be understood at a fundamental level. Here we demonstrate a new scanning probe based technique: torsional resonance nanoimpedance microscopy (TR-NIM), which simultaneously probes transport and dielectric properties in conjunction with optical excitation. To make a controlled interface, we start by designing a peptide molecule with ability to control protein/electrode interface interactions, as well as incorporation of several different optically active cofactors, and we successfully patterned peptides on HOPG substrates. Using TR-NIM electronic transport and the effect of optical absorption on dielectric polarizability in oriented peptide single or multiple molecular layers is determined. This approach enables quantitative comparisons of the change in polarization volume between the ground state and excited state in both single and multiple molecular layers.

11:00am **AS+BI+NS-WeM10 Scanning Local Capacitance Measurements with High Spatial and Dielectric Resolution.** *M.J. Brukman, S. Nanayakkara, D.A. Bonnell*, University of Pennsylvania

Spatial variation of dielectric properties often dictates the behavior of devices ranging

from field effect transistors to memory devices to organic electronics, yet dielectric

properties are rarely characterized locally. We present methods of analyzing 2nd

harmonic-based local capacitance measurements achieved through non-contact atomic

force microscopy. Unlike contact-based methods, this technique preserves tip

shape and allows the same probe to realize high-resolution topographic imaging and

scanning surface potential imaging. We present an improved analysis of the electrical

fields between tip and sample, yielding high sensitivity to the capacitance-induced

frequency shift.

The techniques are applied to thin-film strontium titanate and mixed-phase self-

assembled monolayers to illustrate application to high dielectric constant hard materials

and lower dielectric constant organic films. Conversion from frequency shift signal to

dielectric constant  $\kappa$  is demonstrated on both samples, with sub-5 nm spatial resolution

and dielectric constant resolution between 0.25 and 1.

11:20am **AS+BI+NS-WeM11 Parallel Momentum Conservation of Hot Electrons across a Metal Semiconductor Interface.** *J.J. Garramone, J. Abel, R. Balsano, V.P. LaBella*, College of Nanoscale Science and Engineering, the University at Albany-SUNY

Parallel momentum of electrons is a conserved quantity as the electron traverses a barrier between two materials which lead to refraction like effects in the electrons trajectories. Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) based technique that injects hot electrons ( $E > EF$ ) into a metal-semiconductor Schottky diode<sup>[1]</sup>. A small fraction of these electrons will traverse the metal with little to no scattering and make it into the semiconductor and counted as BEEM current. This makes it an ideal technique to study parallel momentum conservation. However, direct observation of this effect has been rather elusive. To observe this effect the dependence of the attenuation length with hot electron energy of Ag on both the Si(001) and Si(111) substrates has been measured.

Samples consisted of nanometer thick Ag films that were deposited on HF cleaned Si(001) and Si(111) wafers and capped with 10 nm Au to prevent oxidation of the films. Attenuation lengths were extracted by measuring the BEEM current as a function of the metal overlayer thickness. The dependence of the attenuation length with tip bias (electron energy) displayed a sharp increase as the energy approached the Schottky barrier height for the Si(001) substrates and a slight decrease for the Si(111)

substrates. This contrast is a direct result of parallel momentum conservation and the lack of zero parallel momentum states at the Si(111) interface when compared to the Si(001) interface. Additional insight into the relative contribution of both elastic and inelastic scattering can be obtained by fitting the data to a Fermi liquid based model.

[1] L. D. Bell, et al., Phys. Rev. Lett. **61** 2368 (1988).

11:40am **AS+BI+NS-WeM12 High Resolution Scanning Probe Imaging of 2D-Supramolecular Networks on Au(111), Graphite and Molybdenite.** *V.V. Korolkov, S. Allen, C.J. Roberts, S.J.B. Tendler*, The University of Nottingham, UK

Chemical decoration of surfaces with various molecules and supramolecular structures has been a major strategy for introducing new properties to both organic and inorganic materials. Amongst these properties are wettability, biocompatibility, sensing properties, catalytic activity, optical properties and adhesion. Most of methods for surface modification include molecules binding to the surface via stable chemical bond. Recently methods have been developed to modify atomically flat surfaces with periodical porous molecular structures, termed 2D-supramolecular networks. The networks are commonly composed of two types of molecules serving different functions e.g. joints and ribbons. Such 2D-structures bring forward a unique surface property - a spatially controlled adsorption with almost single molecule precision.

Most networks reported in the literature have been studied using UHV STM on metal substrates and, to a lesser extent, on HOPG and non-conductive substrates. Here we present a study, utilizing both ambient STM and AFM, of 3,4,9,10-perylene-tetracarboxylic diimide (PTCDI) - melamine networks deposited on Au(111), HOPG and MoS<sub>2</sub> substrates. AFM imaging was performed using PeakForce Tapping AFM (Bruker Inc.) and Torsion Resonance (TR)-AFM. Both STM and AFM were able to resolve a clear periodical network structure for all substrates after exposure to a solution of PTCDI and melamine molecules in dimethylformamide at 373K. AFM images show that the network forms a monolayer on both HOPG and molybdenite substrates, and also that most of the HOPG surface is covered with network structure, with some minor defects. In contrast the Au(111) surface was mostly covered with network multilayers as suggested both by TR-AFM and STM. AFM also revealed that the network structure on HOPG and molybdenite remains intact for several hours in the ambient and can be stored in N<sub>2</sub>-ambient for up to ~24h.

## Helium Ion Microscopy Focus Topic Room: 106 - Session HI+AS+BI+NS-WeM

### Nano- and Bio- Imaging with Helium Ion Microscopy

**Moderator:** A. Götzhäuser, University of Bielefeld, Germany, V.S. Smentkowski, GE-GRC

8:40am **HI+AS+BI+NS-WeM3 Helium Ion Microscopy Techniques for Imaging and Characterization of nano-Device Materials and Structures.** *S. Ogawa, T. Iijima*, National Institute of Advanced Industrial Science and Technology (AIST), Japan **INVITED**

This paper presents several imaging modes for nano-devices fabrication that may make HIM a tool of particular value to soft materials such as low-k dielectrics (low-k) with less transformation and more materials contrast which reflects damaged areas, and copper interconnect buried in dielectrics, and shows luminescence induced by the focused helium ion beam using the HIM for the first time.

Imaging of -100 nm pitch patterned low-k is important for LSI Cu/low-k interconnect processes, while SEM imaging results in changes to the low-k line edge roughness and shape by damage during an electron beam irradiation. The HIM could provide low-k dielectric secondary electron (SE) image with nm order resolution, deeper focus depth, less transformation because of three order magnitude lower thermal energy transfer into a unit volume of the low-k than the SEM under an appropriate operation condition<sup>1)</sup>.

During the imaging, even at very low helium ion current, surfaces of samples were atomically etched off, as in a graphene patterning, and then blistering or physical etch occurred with the increase of the helium ion current. This makes the interpretation of the HIM SE imaging difficult but helpful. Damaged areas at side walls of the low-k regions in a 140 nm pitch interconnect were successfully seen with a different contrast from non-damaged low-k regions at an "optimized" helium ion beam condition<sup>2)</sup>, which was similar to a TEM/Valence EELS result. On the other hand, using

the SEM, the damaged areas contrast in the low-k regions could not be imaged.

A new imaging mode, through the inter-level dielectric, of the underlying copper, was explored. Cu interconnect was seen through a 130 nm thick low-k dielectrics. The incident helium ions might generate secondary electrons (SEs) at the buried Cu surface and the SEs of 1-2 eV energy passed through the dielectric of a few eV band gap without any energy transfer, and then the image was obtained. Helium ion channeling at the Cu surface area varied the secondary electron quantity, and it might generate a crystal orientation contrast of the buried Cu metal.

Luminescence induced by the focused helium ion beam was studied using the HIM<sup>2</sup>. Helium ion beam of a few pA current was irradiated to a SiO<sub>2</sub> film, and peaks in a spectrum were observed at around 281, 447, and 672 nm; these positions were different from those by a conventional SEM cathode luminescence. The further study will be presented.

L.Stern, W.Thompson and J.Notte of Carl Zeiss are acknowledged for their discussions in the Cu / low-k works.

1) S. Ogawa, et al, Jpn. J. Appl. Phys., 49 (2010) 04DB12, 2) S. Ogawa, et al, Proc. of 2011 IEEE IITC (2011)

9:20am **HI+AS+BI+NS-WeM5 He Ions Image the Au (111) Herringbone Reconstruction.** *V. Veligura, G. Hlawacek, R. van Gastel, H. Zandvliet, B. Poelsema*, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

The herringbone reconstruction of the Au(111) surface was directly visualized using an Ultra High Vacuum Helium Ion Microscope. Ion channeling phenomena arise from the different atomic ordering in the outermost layer of the crystal. First, we investigated the channeling contrast from the bulk Au fcc structure by imaging polycrystalline Au on glass films. The contrast that was observed as a function of crystal orientation was found to conform to what is calculated from a simple hard sphere model. Consequently, the herringbone reconstruction was investigated. It is a periodic zigzag structure of the three different types of crystal stacking (fcc, hcp and bridge sites connecting these regions) and, ideally, has a period of 6.3 nm. The different stacking of the atoms that constitute the surface reconstruction leads to lateral variations of the secondary electron yield that can be resolved in HIM imagery. The existence of the herringbone reconstruction on the sample was independently confirmed through STM measurements and the quantitative details from both techniques are similar, but seem to be affected by the differences in vacuum conditions. An influence of both the ion beam and vacuum environment on the visibility of the herringbone reconstruction is observed in our UHV-HIM system.

9:40am **HI+AS+BI+NS-WeM6 Imaging of Graphenoid Nanomembranes with Helium-Ion Microscopy.** *A. Beyer, A. Turchanin, A. Götzhäuser*, University of Bielefeld, Germany

Helium-ion microscopy is known for its high surface sensitivity. Here we present a study about imaging extremely thin nano-scale objects: graphenoid nanomembranes which consist exclusively of atoms near the surface. Such freestanding nanomembranes with a thickness of 1 nm are made from self-assembled monolayers (SAMs) by cross-linking and subsequent transfer to transmission electron microscopy (TEM) grids or other suitable substrates. We show that these nanomembranes exhibit a substantially higher contrast in helium-ion microscopes as compared to electron microscopes.

Cross-linking of SAMs is performed by large area exposures with electrons or photons which yield extended nanomembranes. On the other hand, patterned exposures allow the fabrication of nanosieves, i.e. perforated nanomembranes. Advantages in imaging such patterned cross-linked SAMs as well as freestanding nanosieves with the helium-ion microscope will be discussed.

10:40am **HI+AS+BI+NS-WeM9 Nanofabrication and Biological Imaging with the Helium Ion Microscope.** *D.S. Pickard*, National University of Singapore **INVITED**

The Helium Ion Microscope (HIM) is a new imaging technology based on a high brightness and stable Gas Field Ion Source (GFIS). The GFIS employed exhibits a low energy spread (<1 eV), small virtual source size (< 0.3 nm) and a high brightness > 4 x 10<sup>9</sup> A/cm<sup>2</sup>.sr [1]. This, in conjunction with the shallow escape depth (<1 nm) of the secondary electrons generated by the incident 30 keV helium ions, contribute to the HIM's primary advantage in the imaging of solid samples: its high spatial resolution (0.25 nm) [2]. We have applied this novel technology across a broad spectrum of multidisciplinary applications (from basic materials science and semiconductor applications to the biological sciences) to assess its utility and possible advantages over alternative techniques.

One area where our investigations have gained significant traction is in the imaging of biological specimens. The utility of this instrument in addressing topics of the biological sciences is due in part to the HIM's high spatial resolution. However, in the context of biological specimens, it is the ability to image non-conductive samples without the application of a metal (or other conductive) overcoat and without the need of a background gas (both of which degrade resolution and surface details), which has proven to be a distinguishing attribute. This opens up a whole new range of biological problems that can be solved rapidly and with less risk of artifacts.

An equally compelling application is in the field of nano-structuring. The focused helium ions have the ability to directly modify the sample surface under a high ion flux (via surface sputtering). This enables the direct patterning of structures and promises great utility in the fabrication of sub-10 nm devices. It also provides a mechanism for high resolution patterning on nonconventional substrates (such as suspended graphene membranes), where resist-based lithographic techniques are not feasible. Our experiences in sub-10 nm pattern transfer for both graphene and plasmonics applications will be presented.

1. B. Ward, J. Notte, and N. Economou, J. Vac. Sci. Technol. B, Vol. 24, No. 6, Nov/Dec 2006

2. Application Note, Carl Zeiss SMT, "Ultra-High Resolution Imaging in ORION<sup>®</sup>PLUS", PI No. 0220-2008-ENG, Nov. 21, 2008

11:20am **HI+AS+BI+NS-WeM11 Imaging and Characterizing Cellular Interaction of Nanoparticles using Helium Ion Microscopy.** *B.W. Arey, V. Shutthanandan, Y. Xie, A. Tolic, G. Orr*, Pacific Northwest National Laboratory

The helium ion microscope (HeIM) probes light elements (e.g. C, N, O, P) with high contrast due to the large variation in secondary electron yield, which minimizes the necessity of specimen staining. A defining characteristic of HIM is its remarkable capability to neutralize charge by the implementation of an electron flood gun, which eliminates the need for coating non-conductive specimens for imaging at high resolution. In addition, the small convergence angle in HeIM offers a large depth of field (~5x FE-SEM), enabling tall structures to be viewed in focus within a single image. Taking advantage of these capabilities, we investigate the interactions of engineered nanoparticles (NPs) at the surface of alveolar type II epithelial cells grown in culture. The increasing use of nanomaterials in a wide range of commercial applications has the potential to increase human exposure to these materials, but the impact of such exposure on human health is still unclear. One of the main routes of exposure is the respiratory tract, where alveolar epithelial cells present a vulnerable target. Since the cellular interactions of NPs govern the cellular response and ultimately determine the impact on human health, our studies will help delineating relationships between particle properties and cellular interactions and response to better evaluate NP toxicity or biocompatibility.

The Rutherford backscattered ion (RBI) is a helium ions imaging mode, which backscatters helium ions from every element except hydrogen, with a backscatter yield that depends on the atomic number of the target. Energy-sensitive backscatter analysis is being developed, which when combined with RBI image information, support elemental identification at helium ion submicron resolution. This capability will enable distinguishing NPs from cell surface structures with nanometer resolution.

11:40am **HI+AS+BI+NS-WeM12 Application of Helium Ion Microscope on Semiconductor Surface Imaging and Metrology.** *H.X. Guo*, National Institute for Materials Science, Japan, *H. Itoh*, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *K. Onishi, T. Iwasaki, D. Fujita*, National Institute for Materials Science, Japan

Scanning electron microscope (SEM) has been used in the semiconductor surface imaging and metrology for more than 50 years. Now, a new tool, Helium ion microscope (HeIM), is developed and applied to this work. SEM and HeIM are the same in some fundamental characteristics. But, the latter has advantages in smaller probe size, higher resolution, and greater depth of field. These abilities enhance the performance of the HeIM in the semiconductor surface imaging and metrology, such as imaging of low-k materials [1] and measurement of critical dimension of the semiconductor devices [2].

A standard sample for scanning probe microscope tip characterization [3, 4] was measured by using HeIM and atomic force microscope (AFM) as shown in Fig. 1 and Fig. 2. Line profile of the HeIM image in Fig. 1 shows high accuracy in edge definition of the sample. The contrast of the image is related to morphology and materials of the sample [5], the probe size of the Helium ion beam, direction of the sample and beam, charge distribution, and so on. All the aspects will be analyzed in our presentation. The AFM image of the sample shown in Fig. 2 is a dilation of the real surface topography of the sample due to the finite-size AFM tip [6]. With an erosion algorithm, the surface of the sample was reconstructed to be compared with HeIM measurement.

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## Neutron Scattering Focus Topic

**Room: 207 - Session NT+AS+MI-WeM**

### Applications of Neutron Scattering I

**Moderator:** V. Lauter, Oak Ridge National Laboratory

8:00am **NT+AS+MI-WeM1 A Deeper Look into Spintronic Material Systems with Neutrons and Synchrotron Radiation**, *T. Brueckel*, Forschungszentrum Jülich, Germany **INVITED**

The discovery of the Giant Magnetoresistance GMR effect triggered the evolution of Spintronics, i.e. information storage, information processing and information transport using the spin of the electron. While the first Spintronic devices were merely transition metal multilayers, the interest has shifted to include transition metal oxide systems, laterally structured films and magnetic nanoparticles. Scattering techniques applied to model systems are ideal to provide fundamental microscopic information on the spin and domain structure.

In this contribution, we will give an overview highlighting the capabilities of modern neutron and synchrotron x-ray techniques. We will show that neutron scattering under grazing incidence is able to provide unique depth resolved information on magnetization, magnetic correlations and magnetization dynamics relevant for basic and applied research on nanostructured magnetic materials and how synchrotron x-ray scattering can provide complementary element specific information. Examples for current research on patterned metallic multilayers, thin transition metal oxide films and magnetic nanoparticles will be given.

8:40am **NT+AS+MI-WeM3 Magnetic Properties of FePtRh Films and Multilayers Studied by Neutron Scattering**, *D. Lott, J. Fenske*, Helmholtz-Zentrum Geesthacht, Germany, *G.J. Mankey*, Univ. of Alabama, *W. Schmidt, K. Schmalz*, Forschungszentrum Juelich, Germany, *E. Tartakowskaya*, National Academy of Science, Ukraine, *H. Amabye*, ORNL, *F. Klose, A. Mulders*, ANSTO, Menai, Australia, *A. Schreyer*, Helmholtz-Zentrum Geesthacht, Germany, *V. Lauter*, ORNL

Ordered FePt alloys with L1<sub>0</sub> structure are known as materials with FM order and a high magnetic moment of Fe providing a large magnetization. The large atomic number of Pt on the other hand results in a high magnetic anisotropy. If grown in thin films, the high anisotropy often results in perpendicular magnetization which is the preferred orientation for current magnetic recording media. One way to control the magnetic properties in these materials is through the introduction of a third element into the crystal matrix e.g. Rh. When Rh is added to replace Pt in the equiatomic alloy, new magnetic phases emerge. Here neutron diffraction studies on the magnetic properties of different thick Fe<sub>50</sub>Pt<sub>50-x</sub>Rh<sub>x</sub> films in dependence on temperature and external magnetic fields allowed us to investigate the rich phase diagram of the system for thin films, e.g. the transition from the FM to AF state in the system with increasing Rh concentration. In particular films with a Rh concentration of about 10% show a temperature dependent AF-FM transition. From the neutron data it was moreover possible to determine the magnetic configurations in dependence on concentration, temperature and magnetic field on a microscopic scale. Based on the observed results a theoretical model considering the changes in the anisotropies could be developed. In a next step magnetic multilayer consisting of Fe<sub>50</sub>Pt<sub>50-x</sub>Rh<sub>x</sub> bilayers with different Rh concentrations were grown and studied by polarized neutron reflectivity to investigate the magnetic interactions along the lattice matched interfaces. First results will be presented here.

9:00am **NT+AS+MI-WeM4 Spectroscopic and Magnetic Characterization of the Spin-Crossover Transition in Thin Films of Fe(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>(NCS)<sub>2</sub>**, *E.C. Ellingsworth*, *G.J. Szulcowski*, The University of Alabama, Tuscaloosa, *V. Lauter*, Oak Ridge National Laboratory  
The octahedral complex bis(1,10-phenanthroline)dithiocyanate iron(II), Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>, is known

to exhibit an abrupt transition between a high and low magnetic spin state from 170 – 180 K in the

bulk phase. As a result, Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> is an interesting organic semiconductor to study charge and

spin transport in thin films. We synthesized and characterized Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> according to literature

procedures. Thin films of Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> were made by vapor deposition onto a variety of substrates

including Si, KBr, Au and Al and characterized by infrared and photoelectron spectroscopy, SQUID

magnetometry, optical microscopy, and polarized neutron reflectometry. The films were found to be

very sensitive to water vapor under ambient conditions, which complicates the structural, chemical and

magnetic analysis of the films. However, appropriate capping layers can be deposited onto the

Fe(phen)<sub>2</sub>(NCS)<sub>2</sub> thin films to protect them from water vapor before removal from the vacuum system. The

differences in the magnetic behavior of the thin films will be compared to the bulk phase.

9:20am **NT+AS+MI-WeM5 Nanoscopic Magnetic Phase Separation at the SrTiO<sub>3</sub>(001)/La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> Interface**, *M. Sharma*, *M.A. Torija*, Univ. of Minnesota, *J. Gazquez*, *M. Varela*, ORNL, *J. Schmitt*, *C. He*, Univ. of Minnesota, *J.A. Borchers*, *M. Laver*, NIST, *S. El-Khatib*, American University of Sharjah, *V. Lauter*, *H. Ambaye*, *R. Goyette*, ORNL, *C. Leighton*, Univ. of Minnesota **INVITED**

The remarkable functionality of complex oxides, when combined with the favorable lattice matching that is possible at their interfaces, provides many opportunities for new physics and applications. The perovskite manganites and cobaltites are excellent examples, being of interest in gas sensing, catalysis, and as electrodes in ferroelectric memory and solid oxide fuel cells. From the magnetism perspective they have potential for high conduction electron spin polarization, and a variety of functional ground states. However, the same delicate balance between phases that provides such impressive functionality also leads to a serious problem; it can be difficult to maintain desired properties (e.g. high spin polarization and conductivity) close to the interface with a dissimilar oxide. This is exemplified by magnetic tunnel junctions for example, where the interface spin polarization is suppressed and drops rapidly with temperature. In this work, using SrTiO<sub>3</sub>(001)/La<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> [1] as a model system, we have combined epitaxial growth by high pressure oxygen sputtering with atomic-level structural characterization (including STEM/EELS imaging [2]), conventional magnetometry, electronic transport, small-angle neutron scattering, and polarized neutron reflectometry. We observe the usual degradation in magnetization and conductivity in the very thin film limit. We demonstrate that this is due to nanoscopic magneto-electronic phase separation in the interface region [3]. Essentially, nanoscopic ferromagnetic (FM) clusters form in an insulating non-FM matrix near the interface, resulting in reduced magnetization and conductivity, even at compositions that display no such phase separation in bulk. STEM/EELS depth profiling of the chemical composition reveals that this effect has a chemical origin, being due to subtle depth-wise variations in Sr and O content, resulting in reduced hole doping near the interface. Simple thermodynamic and structural arguments for the origin of these variations are provided, based on Sr dissolution energies and the critical link between strain state and O vacancy concentration provided by O vacancy ordering [2,3].

Work at UMN supported by NSF and DoE (neutron scattering). Work at ORNL supported by DoE. Work at UCM supported by the European Research Council.

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10:40am **NT+AS+MI-WeM9 Study of L1<sub>0</sub> Ordering in <sup>57</sup>Fe/Pt Multilayers**, *K. Srikanti*, Ugc-Dae, Csr, India

Ordered L1<sub>0</sub> FePt, FePd and CoPt alloy thin films have large magnetic anisotropy constants suitable for high-density recording media. The L1<sub>0</sub> ordered phase is obtained with post growth annealing at high temperatures. However, the high temperature annealing leads to grain growth. The present

work is an attempt to lower the transition temperature starting with multilayer precursors. The evolution of the structural and magnetic properties of Si(sub) [<sup>57</sup>Fe(19Å

)Pt (25Å)]<sub>x10</sub> multilayers as a function of vacuum annealing at different temperatures is studied. The film thickness is selected to have equi-atomic stoichiometry. The multilayers are prepared by ion beam sputtering. X-ray reflectivity (XRR), X-ray diffraction (XRD), and magneto optical Kerr effect (MOKE) and conversion electron Mössbauer spectroscopy (CEMS) are used to characterise the as-deposited and annealed multilayers. Using XRR it is observed that due to intermixing FePt alloy formation takes place with annealing. The XRD indicated the presence of superstructure peaks at 350°C and above. Mössbauer measurements indicated a clear evidence for the strong exchange coupling between the soft fcc FePt and hard fct FePt phase. The results indicate that the multilayer structure does not transform directly to the ordered fct FePt, rather first an fcc FePt phase is formed and subsequently it gets converted in to the fct FePt phase as a function of annealing. A detailed study on stoichiometric FePt system embedded in Carbon matrix prepared by ion beam sputtering technique will also be discussed.

Few preliminary results of polarised neutron reflectivity measurements on FePt/FeNi exchange spring magnets will be discussed.

11:00am **NT+AS+MI-WeM10 Influence of Capping Layer Rigidity on Properties of Supporting Temperature Sensitive Hydrogel Polymers Using Neutron Reflectivity.** *M. Dubey*, Los Alamos National Laboratory, *M.S. Jablin*, Carnegie Mellon University, *M. Zhernenkov*, Los Alamos National Laboratory, *R. Toomey*, University of South Florida, *J. Majewski*, Los Alamos National Laboratory

Temperature sensitive hydrogel polymers are utilized as responsive layers in various applications. While the polymer's native characteristics have been studied extensively, details concerning its properties during interaction with bio-related structures are lacking. This work investigates the interaction between a thermoresponsive polymer cushion and different lipid membrane capping layers probed by neutron reflectometry. N-isopropylacrylamide copolymerized with methacryloylbenzophenone first supported a lipid bilayer composed of 1,2-Dipalmitoyl-*sn*-Glycero-3-Phosphoethanolamine (DPPE) and subsequently 1,2-Dipalmitoyl-*sn*-Glycero-3-Phosphocholine (DPPC). The polymer-membrane systems were investigated above and below the polymer lower critical solution temperature (37 and 25 °C). While the same cushion supported each lipid membrane, the polymer hydration profile and thickness were markedly different for DPPE and DPPC systems. Since DPPE and DPPC have different bending rigidities, these results establish that the polymer-membrane interaction is critically mediated by the mechanics of the membrane, providing better insight into cell-hydrogel interactions. There has been increased interest in the effect of matrix elasticity on cell lineage specification. Polymeric matrices with known stiffness are utilized as supports to understand the physical effects of *in vivo* tissue microenvironment for therapeutic uses of stem cells. This work focuses on the influence of a capping layer on the mechanical properties of the underlying support.

# Wednesday Afternoon, November 2, 2011

Applied Surface Science Division

Room: 102 - Session AS-WeA

## Correlative Analysis - A Multi-technique Approach for Identification and Structure-Property Relationships

Moderator: K. Artyushkova, The University of New Mexico

2:00pm **AS-WeA1 Complementary Ultra Thin Film Analysis using Low Energy Ion Scattering (LEIS) and TOF-SIMS**, T. Grehl, P. Bruener, ION-TOF GmbH, Germany, N. Havercroft, ION-TOF USA, Inc., H. Brongersma, E. Niehuis, ION-TOF GmbH, Germany

Ultra-thin film structures have become increasingly important and simultaneously gained complexity with regard to the number of layers and the elemental composition. Understanding the processes occurring during deposition is crucial for improving the film quality. Especially during the first stages of film growth, analytical techniques with high surface sensitivity and good detection limits are required to study the growth process.

Low Energy Ion Scattering (LEIS) lends itself well to these tasks with its ultimate surface sensitivity of a single monolayer and detection limits of down to 10 ppm. This is accomplished by bombarding the surface with noble gas ions of a few keV and measuring the energy loss of the backscattered ions at a fixed scattering angle. The energy spectrum is converted into a mass spectrum of the elements present at the sample surface. The absence of matrix effects allows a straightforward quantification.

Besides the composition analysis of the outermost atomic layer, depth profiling is available via two distinct methods. Static depth profiling exploits the fact that ions scattered in deeper layers lose additional energy proportional to the penetration depth. As this process involves neutralization and re-ionization, intensities are lower than for the ions scattered at the surface. Thus, these ions can be distinguished, giving information about the elemental distribution in the first few nm in a non-destructive way. Alternatively, dynamic depth profiling is available by using a second, low energy sputter ion beam to erode the surface while recording surface spectra at different depths. This yields a quantitative, high depth resolution depth profile. By observing the change in the in-depth signal during sputtering, the sputter rate can be intrinsically and continuously determined.

The unique advantages of LEIS complement established techniques like TOF-SIMS. The latter is often hampered by sputter transients at interfaces and difficult quantification especially of matrix species, but excels as far as the detection of trace elements or the gaining of chemical composition information is concerned. We applied both LEIS depth profiling modes to a number of thin film sample systems. Hereby we show the possibilities arising from each of the two modes, as well as from the combination with TOF-SIMS. Specifically, we worked on model samples relevant to the semiconductor industry (high-k, SiGe). Some of these samples were designed for studying the response function of the in-depth signal in order to improve the understanding and to allow the application to real-world samples, e. g. to correct for varying erosion rates.

2:20pm **AS-WeA2 Multi-technique Characterization of Polymer Surfaces and Diamond-Like Carbon Films**, P. Mack, R.G. White, A.E. Wright, Thermo Fisher Scientific, UK

Surface treatment of polymers produces materials that exhibit a wide range of surface compositions, properties and structures. The chemical and structural properties of these novel materials can be exploited for the fabrication of devices for bio-medical and electronics applications. Additionally, the wear-resistant properties of steel can be modified by coating the surface with a diamond-like carbon (DLC) film.

The combination of a variety of complementary surface-sensitive electron spectroscopies maximises the information available to the analyst for full quantitative surface characterisation of polymer surfaces and DLC films. The silicon content of a DLC film can affect its hardness, for example, and XPS is the ideal technique for chemical quantification of the silicon. The concentration of hydrogen in a DLC film also modifies its wear properties, but XPS cannot quantify this element. It is possible, however, to detect and quantify hydrogen using Reflected Electron Energy Loss Spectroscopy (REELS). When used together, XPS and REELS can provide a total quantification for polymer surfaces and DLC films.

This presentation will show how Thermo Scientific tools can be used to investigate the chemistry and structure of various polymer and DLC samples. Chemical changes produced by surface treatments were examined by high energy resolution XPS and argon profiling (both monomer and gas cluster). Complementary REELS measurements were used to examine the level of carbon unsaturation at the uppermost surface of each sample and to detect and quantify hydrogen.

2:40pm **AS-WeA3 Challenges Associated with Mathematically Correlating Data from Multiple Surface Characterization Techniques**, K.G. Lloyd, D.J. Walls, L. Zhang, J.P. Wyre, DuPont Corporate Center for Analytical Sciences **INVITED**

There are now many examples of multivariate analysis of surface-specific technique data[1,2]. These include multivariate statistical methods such as Principal Components Analysis (PCA), Partial Least Squares (PLS), or Multivariate Curve Resolution (MCR) applied to so-called "hyperspectral" mapping data, in which hundreds of channels of spectral data are collected at each pixel of a two-dimensional pixel array spanning an area of interest. The idea of trying to mathematically correlate different sets of mapping data from the same area is not new[3], and falls under the broader category of 'image fusion' used in conjunction with remote sensing applications[4]. However, this approach is not prevalent in the surface science literature, with the notable exception of Fulghum and Artyushkova[5,6].

There are good reasons for this, from both the experimental and modeling perspectives. This talk will discuss the challenges associated with mathematically correlating spectroscopic and mapping data from multiple surface-specific techniques. Examples from the literature and the analytical lab will be discussed.

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4:00pm **AS-WeA7 Multi-technique Characterization for Interfacial Analysis, Depth Profile and Chemical Imaging**, S.V.N.T. Kuchibhalla, V. Shutthanandan, B.W. Arey, C.M. Wang, M.I. Nandasiri, N. Ponnusamy, T. Varga, S. Thevuthasan, Pacific Northwest National Laboratory, F. Liu, L. Huang, L. Porter, R.F. Davis, Carnegie Mellon University, T. Prosa, CAMECA Instruments Inc.

Nanoscale interfaces are finding use in a multitude of applications including fuel cells, LEDs etc. In addition, our group at EMSL, Pacific Northwest National Laboratory is interested in understanding the influence of interfaces on energy and environmental applications, in particular, radiation tolerance, and oxygen ion conduction. While a number of techniques are available to synthesize interfaces, their analysis is often challenging. Hence, the fundamental understanding required to develop next generation devices with controlled interfaces is not widely available in the literature. In this context, it is imperative to intelligently combine more than one analytical technique and as appropriate use new techniques with improved spatial and chemical resolutions (better chemical sensitivity and improved mass resolution) to achieve such a goal. Atom Probe Tomography (APT), a relatively new technique that complements various surface and interfacial analysis tools, is capable of providing 3D-chemical images of various materials including multi-layer thin films with sub-nanometer spatial and a ppm level chemical resolution. This talk will focus on combining the information obtained from high-resolution scanning transmission electron microscopy, high-resolution Rutherford backscattering spectrometry, x-ray photoelectron spectroscopy, atom probe tomography, x-ray reflectivity and diffraction analysis of two sets of multi-layer thin films. The first set of multi-layer thin films is synthesized using oxygen plasma-assisted molecular beam epitaxy consisting of samaria doped cerium oxide and scandia stabilized zirconium oxide. These films are expected to provide significantly enhanced oxygen-ion conduction relative to the films that are made of either of the materials. The second set of films, consisting of GaN, InGaN multi-quantum well structures, is prepared using metal-organic

chemical vapor deposition. These structures as green LED active regions were shown to have significant improvements in internal quantum efficiency when employing an InGaN buffer layer to modulate MQW interface roughness. The information such as layer thickness, elemental composition of the layers and interfacial roughness/mixing would be compared from various techniques mentioned earlier. Dopant distribution and any possible intermixing of the layers will be of major interest in the case of ceria-zirconia system. The interfacial roughness and any preferential segregation or clustering of In along with 2D/3D uniformity of the layers will be of most interest in the GaN-InGaN system.

**4:20pm AS-WeA8 Characterization of Lubricant Coated Cartridges Using Multiple Surface Analytical Techniques, X. Dong, Z. Xiao, C. Kemp, Eli Lilly and Company**

Glide force is a key performance attribute for pharmaceutical injection devices. It is directly impacted by lubricant amount, lubricant distribution, and surface chemistry. However, obtaining accurate information on these lubricant properties has been a challenge within the industry because all of the surfaces are curved. Although ellipsometry has been routinely applied to measure the thickness of individual layers within flat samples, the analysis of multi-layered, curved samples, especially non-destructively, remains difficult. We have modified the sample stage and sample holder of a conventional ellipsometer to make it possible to examine lubricant distribution within drug containers with different geometric configurations and components, including those made of plastic and glass. To overcome the challenge introduced by curved surface, the area of the surface analyzed in any individual experiment is reduced to allow effective focusing of the beam. The mapping of large, curved areas may then be accomplished by assembling multiple individual analyses. The relationship between sprayed volume and lubricant thickness can thus be established through non-destructive analysis by ellipsometry. The surface chemistry of a fluorine containing lubricant was evaluated by FTIR-ATR and XPS, both before and after post-spray treatment. Fluorine concentration remains stable with mild treatment, but lubricant was depleted from the surface after severe treatment. This work demonstrated that the combination of multiple surface analytical tools can enhance our understanding of the device lubrication process.

**4:40pm AS-WeA9 Challenges in Surface and Interface Analysis of Thin Films, H. Piao, General Electric Co., Y.F. Hu, Canadian Light Source Inc., Canada, J. Fronheiser, General Electric Co., V. Tilak, General Electric Co., India, M. Karadge, M. Morra, General Electric Co.**

Surface analysis methods play an important role in the characterization of thin films. The analysis of "nano-structured" films requires further development of existing surface analysis methods and exploration of new techniques. The aim of this presentation is to identify some of the challenges that exist in understanding surface and interface states of thin films using conventional X-ray Photoelectron Spectroscopy (XPS). Unique advances in thin film analysis using synchrotron-based X-ray Photoemission (XPS) and X-ray Absorption Near Edge Structure (XANES in both TEY and FLY modes) techniques are discussed. The presentation gives an emphasis on how these methods complement each other. Examples describing the characterization of thin films are given in two areas of technology that are growing in importance: (1) Gate oxide development on SiC and (2) corrosion inhibitor coatings.

**5:00pm AS-WeA10 A Comparison of AES and XPS Depth Profiling for Characterization of Multicomponent Thin Films, B.R. Rogers, R.R. Harl, Vanderbilt University**

Auger electron spectroscopy (AES) depth profiling has been used to characterize thin films for decades. Thin film depth profiling using x-ray photoelectron spectroscopy (XPS) has become increasingly common due to recent advances in XPS instrumentation. Often the choice of which depth-technique is best for a particular sample is not clear. In this presentation I will compare the logistics and results of AES and XPS depth profiling of insulating and metallic multicomponent thin films. Depth profiles of  $\text{SiO}_x\text{C}_y$  and  $\text{CrSi}_x\text{N}_y$  thin films acquired using both techniques will be presented. Sample preparation, analysis set-up, and analysis time will be compared. Signal to noise and interface sharpness of the resulting profiles will be compared. The ability to determine chemical state information from the acquired data will also be discussed.

**5:20pm AS-WeA11 Characterization and Fabrication of Patterned, Infiltrated Carbon Nanotube Forests with Applications to Thin Layer Chromatography, M.R. Linford, D. Jensen, R. Davis, S. Kanyal, Brigham Young University, A. Dadson, M. Vail, US Synthetic Corporation**

Patterned forests of carbon nanotubes (CNTs) were used as a template to fabricate novel silica-based thin-layer chromatography plates (TLC). The resulting CNTs are infiltrated with elemental silicon by low pressure

chemical vapor deposition of silane. Silicon coated CNTs are annealed in air to remove the CNTs and convert the silicon to silica. The resulting material is white, which is indicative and characteristic of silica. This process produces TLC plates that are porous and robust. The microfabricated TLC plates are characterized extensively by scanning electron microscopy (SEM), which shows the precise placement of the adsorbent material. Plates are also characterized by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and BET isotherm measurements. Unlike almost all other commercially available plates, these microfabricated structures do not require a binder to hold the adsorbent material together. Baseline separation of a CAMAG (Muttenez, Switzerland) five-component dye test mixture using toluene as the mobile phase was obtained. The chromatographic efficiencies of these microfabricated TLC plates are typically 70% higher than commercially available high-performance TLC plates, and sometimes much higher, also showing a 150% reduction in development time; these microfabricated TLC plates allow for both improved efficiency and speed of analysis.

**Biomaterial Interfaces Division**

**Room: 108 - Session BI+AS+NS+SS-WeA**

**Functionalization and Characterization of Nanostructures**

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

**2:00pm BI+AS+NS+SS-WeA1 Characterization of Nano-objects by Cluster-SIMS, E.A. Schweikert, Texas A&M University INVITED**

Secondary ion mass spectrometry, SIMS is a method of choice for the chemical analysis of nanodomains embedded in solids. We examine here a case which has received little attention, the analysis of individual, free-standing nano-objects. Our approach uses a variant of SIMS. The nano-objects are bombarded with a sequence of individual projectiles resolved in time and space, in the present case  $\text{Au}_{400}^{4+}$  of up to 520 keV impact energy. The successive projectiles impact stochastically the nano-objects dispersed on a solid support. Typically tens of secondary ions are ejected from each impact. They are identified with time-of-flight mass spectrometry and recorded individually. This approach reveals molecules co-located within the 10-20 nm diameter area of emission from one  $\text{Au}_{400}^{4+}$  impact. We demonstrate that the event-by-event bombardment-detection mode is sensitive to the chemical and/or physical nano-scale separation of molecular species. The performance is illustrated with the determination of the relative abundance of the oxide layer in the near surface of 50-100 nm nanoparticles; the nature and abundance of different nano-objects (5-20 nm in diameter) in mixtures of nano-sized solids; the composition of bio-objects such as a bacteriophage including the amino acids of the proteins surrounding the phage and the bases from the encapsulated DNA. The distinct feature of the nanoprobe technique presented here is in the detection of co-emitted ejecta from individual projectile impacts which allows to test chemical composition, in a nonimaging mode, yet at an exquisite level of spatial resolution. Moreover the co-emission of fragment and parent ions enhances the accuracy of molecular identification.

Work supported by NSF grant CHE-0750377

**2:40pm BI+AS+NS+SS-WeA3 Strategies for Studying the Surface Chemistry of Engineered Nanoparticles with SIMS, C. Szakal, J. McCarthy, National Institute of Standards and Technology, K. Louis, R.J. Hamers, University of Wisconsin-Madison, R.D. Holbrook, National Institute of Standards and Technology**

The environmental toxicity of engineered nanoparticles (ENPs) is of increasing importance as these materials become more widely used in manufacturing processes and consumer products. Nanoparticles have extremely high surface-to-volume ratios, which makes the surfaces more critical than their corresponding bulk materials in terms of reactivity, aggregation, and toxicity to various life forms. Therefore, it is critical that we develop methods to distinguish small chemical changes on nanoparticle surfaces in order to understand how these materials will interact outside of controlled laboratories. Conventional approaches of nanoparticle characterization have focused on high resolution morphological imaging (TEM, SEM) and physical property measurements such as surface charge. However, chemical information is generally only inferred from these materials with most current methods. If it is possible to obtain both elemental and molecular information from ENP surfaces, we may be able to determine the eventual fate of ENPs in the environment.

We have developed a comprehensive approach for studying the surface chemistry of ENPs, including 1) preparation of ENPs to controllably surface desired variables, 2) development of methods such as time-of-flight

secondary ion mass spectrometry (ToF-SIMS) and environmental scanning electron microscopy (ESEM) to probe small changes in ENP surface chemistry and/or aggregation, and 3) development of methods to improve the speed and reproducibility of ENP aggregation for batch studies. These approaches will be utilized as the basis of future toxicity studies of selected ecosystems.

**3:00pm BI+AS+NS+SS-WeA4 Unusual Hydrogenation Isotherms for Pd Nanoring Model Systems Observed Via Nanoplasmonic Sensing.** C.B. Langhammer, E.M.K. Larsson, I.L. Zoric, Chalmers University of Technology, Sweden, V.P. Zhdanov, Boreskov Institute of Catalysis, Russian Federation

Nanostructured materials have been proposed as a solution for the development of efficient hydrogen storage systems. As the size of the system gets reduced in the nanometer range enthalpies and entropies of hydrogen dissolution in the metal ( $\alpha$ -phase) and hydride formation ( $\beta$ -phase) as well as activation barriers for diffusion and desorption of hydrogen become size dependent thus influencing both thermodynamics (pressure-composition isotherms) and kinetics (loading/unloading kinetics). The pressure-composition isotherms for a H<sub>2</sub>/M system show a well-known behavior typical for an  $\alpha$ -phase in the low pressure-composition range followed by a plateau signaling the onset of a hydride formation ( $\beta$ -phase) via a first order phase transition and a coexistence of the two over a wide composition range. At higher pressure a pure  $\beta$ -phase exists characterized by a pressure-composition curve with a steep slope. The plateau pressure of the H<sub>2</sub>/M system is determined by the requirement of equilibrium between the three phases in coexistence, thus primarily by the enthalpy and entropy of hydride formation. In case of more than one hydride type a coexistence region exhibits multiple plateaux determined by appropriate energetics as described above. In all known cases the same multiple plateaux features were observed both during the charging and discharging process, i.e. when hydrogen pressure was increased/decreased, accompanied of course by a perennial hysteresis.

In this work we report unusual pressure-composition isotherms for H<sub>2</sub>/Pd nanosized rings where a double plateau isotherms are observed during the charging process and a single plateau one during the hydrogen discharging. The Pd nanorings were fabricated using colloidal lithography. Hydrogen isotherms were followed by monitoring the shift in the ring Localized Surface Plasmon Resonance, LSPR, upon exposing the system to increasing/decreasing hydrogen pressure steps (and equilibrating the sample at each pressure step). The shift of the LSPR resonance was calibrated by preparing the same ring structure on a quartz crystal microbalance and "weighing" directly absorbed hydrogen. A linear relation between the LSPR shift and QCM frequency shift (proportional to hydrogen concentration) was observed.

We present a simple model, based on the observed heterogeneity of the nanorings (as seen in TEM) and by taking into account the defect induced lattice strain, that accounts for the unusual behavior of the observed isotherms.

**4:00pm BI+AS+NS+SS-WeA7 Surface Functionalization and Analysis of Functional "Soft" Nanostructures: From 2 to 3 Dimensions, H. Schönherr,** University of Siegen, Germany **INVITED**

The local properties of soft matter, e.g. for the fabrication of functional biointerfaces or nanostructures, are of tremendous importance for ultimate functionality. In this presentation, the closely interrelated areas of surface chemical functionalization / engineering and analysis of properties will be discussed based on three key examples. These example include: (i) synthesis and modification of polymer brushes with particular focus on the nanomechanical properties, (ii) ultra small diameter nanotubes obtained by the layer-by-layer assembly of polyelectrolytes inside a sacrificial porous template and (iii) block copolymer nanocapsules that are developed for advanced wound management. In all examples, confinement effects are expected to play a significant role in determining e.g. the mechanical properties, as assessed by atomic force microscopy (AFM) nanoindentation.

For thin polymer films (2D) the dependence of the mechanical properties on the film architecture was unraveled. Compared to spin-coated films, brushes synthesized on gold surface by surface initiated polymerization showed higher elastic moduli, which is attributed to entropy effects. Upon chemical crosslinking tunable elastic properties are obtained, which provides interesting pathways for the fabrication of defined cell - surface contacts.

Similarly important are defined nanoscale objects that can be obtained via the replication of small templates by the so-called layer by layer (LbL) deposition of polyelectrolytes (G. Decher Science 1997, 277, 1232). LbL deposition in porous Anodic Aluminum Oxide (AAO) was only very recently expanded to the 100 nm length scale due to an alleged entropic barrier caused by adsorbed polyelectrolytes close to the pore orifice [Y. Cho et al. Small 2010, 6, 23, 2683.]. However, in contrast to this report, we show that the adsorption of polyelectrolytes on the top plane of the AAO and

polymer sedimentation have been identified as main bottlenecks. Suppressing these processes enabled us to produce free standing polymer nanotubes with external diameters of < 55 nm.

Finally, first steps in the development of active nanocapsules filled with a reporter dye or an antimicrobial agent for applications in burn wound management will be presented. In particular the case of burn wounds and the devised biomimetic strategy of BacterioSafe will be introduced. Subsequently, the fabrication and characterization of a polystyrene-block-poly(acrylic acid) amphiphile-based model vesicle system, in particular the loading and release behavior and mechanical properties will be discussed.

**4:40pm BI+AS+NS+SS-WeA9 Large Area Fabrication of Biological Nanostructures,** G. Tizazu, O. El-Zubir, University of Sheffield, UK, S. Brueck, University of New Mexico, D. Lidzey, G. Leggett, University of Sheffield, UK, G.P. Lopez, Duke University

There has been enormous interest in the control of biological interactions at interfaces with nanometer spatial resolution, but important challenges still remain to be addressed. Of the established fabrication techniques, electron beam lithography is expensive, and requires exposure under vacuum, while scanning probe methods are slow and (with few exceptions) do not permit fabrication over large areas. In contrast, interferometric lithography (IL) is a simple approach that uses inexpensive apparatus to fabricate sub-wavelength structures over macroscopic areas. When two coherent laser beams interfere, they yield a sinusoidal pattern of intensity that may be used to modify photosensitive materials. Previously IL has been used extensively for semiconductor nanofabrication, but our recent data show that combined with self-assembled monolayer resists it provides a fast, simple method to create molecular nanostructures over macroscopic areas. Illustrations will be provided of bionanofabrication using interferometric modification of protein-resistant (oligo ethylene glycol) functionalised surfaces, where feature sizes as small as 30 nm ( $\lambda/8$ ) have been achieved over square cm areas, and the controlled growth of protein-resistant brush structures from patterns of initiators for atom-transfer radical polymerisation. The fabrication of metallic nanostructures over macroscopic regions, including Ti structures as small as 35 nm, and gold nanostructures of controlled size and periodicity will also be demonstrated.

**5:00pm BI+AS+NS+SS-WeA10 Functionalization of Mesoporous Silicon Biosensors to Achieve Tunable DNA Bioreceptor Density, J. Lawrie,** R.R. Harl, B.R. Rogers, P. Laibinis, S.M. Weiss, Vanderbilt University

Porous silicon has become a widely studied material for sensing over the last decade based on its large surface to volume ratio and easily tunable morphology. With growing interest in the detection and analysis of genetic material, DNA oligos have become an increasingly important bio-recognition element in porous silicon and many other sensor platforms. As aptamers, nucleic acids serve as high affinity bioreceptors to a wide range of small molecules and biological materials, opening up a number of potential applications in environmental science, chemical and biological defense, and medical diagnostics. In this work, tuning of the porous silicon surface chemistry is described. Controlling surface silanization, bioreceptor density, and bioreceptor charge and secondary structure enables the fabrication of reusable, label-free optical sensors toward specific nucleic acid targets. Detection limits in the nanomolar range have been demonstrated.

We have previously shown that in situ DNA synthesis via the phosphoramidite method in porous silicon produces high bioreceptor coverage for label-free optical biosensing applications. Low hybridization efficiency, despite high sensitivity, for such sensors indicated that tuning the receptor surface density could further improve detection limits. To modify surface receptor density, two-component trichlorosilane monolayers were deposited from solution onto porous silicon. One monolayer component remained active to phosphoramidite chemistry while the second component was inert. This method enabled a range of surface probe densities to be achieved and controlled via silanization conditions. Monolayer composition and DNA receptor density were verified using XPS, contact angle, and UV-Vis spectrophotometry. For a 16mer DNA oligo bound within a porous silicon waveguide, detection of the complementary target nucleic acid was maximized when 25% of the internal pore surface area was active toward DNA synthesis. Tuning surface DNA density increases sensitivity by a factor of 2-3. Label-free, target-specific detection of oligos was observed at concentrations of 25nM.

We will present results from hybridization efficiency studies in which DNA bioreceptor surface density, length, and secondary structure are varied. These parameters are vital to nucleic acid aptamer sensing strategies in label-free optical biosensors. Predicting appropriate receptor surface density for aptamer sensors based upon oligo sequences will provide advantages in achieving fast and sensitive waveguide sensors for detection in complex media.



Acknowledgements: This work is supported in part by the Army Research Office (W911NF-08-1-0200).

5:20pm **BI+AS+NS+SS-WeA11 Composite Fluorocarbon Membranes by Surface-Initiated Polymerization**, C.A. Escobar, A.R. Zulkifli, G.K. Jennings, Vanderbilt University

This presentation describes the fabrication and characterization of a novel composite membrane that consists of two types of nanoporous materials, namely, nanoporous gold leaf (NPGL) and nanoporous alumina, and a selective poly(perfluorohexyl norbornene) (pNBF6) polymer. Integration of the three materials is achieved by means of silane and thiol chemistry, and the use of surface-initiated ring-opening metathesis polymerization (SI-ROMP). The former two provide functionalization of the nanoporous substrates, and the latter promotes the generation of the polymer film within and atop of the alumina-NPGL membrane. The synthetic process is versatile in that simultaneous or selective growth of the polymer film in each nanoporous layer is straightforward. The use of SI-ROMP allows tailoring of the extent of polymerization of pNBF6 throughout the structure by varying polymerization time. Advancing contact angle measurements show that the surface of these composite membranes exhibits both hydrophobic and oleophobic behavior. Scanning electron microscopy (SEM) images indicate that the thin polymer films cover the porous substrates entirely. Results from electrochemical impedance spectroscopy (EIS) confirm that the membranes provide effective barriers to aqueous ions and that sulfonation of the polymer backbone substantially enhances ion transport through the composite membrane. Ion transport and selectivity of the membrane change by regulating the polymerization time. The fluorinated nature of the polymer thin film renders the membrane selective towards molecules with similar chemical characteristics.

## Neutron Scattering Focus Topic

Room: 207 - Session NT+AS-WeA

## Applications of Neutron Scattering II

Moderator: J. Majewski, Los Alamos National Laboratory

3:00pm **NT+AS-WeA4 Probing Fractals by the Combined Ultra-Small- and Small-Angle Neutron Scattering (USANS/SANS) Technique**, M. Agamalian, Oak Ridge National Laboratory

Many natural and man-made materials exhibiting multi-level morphology (atoms – molecules – aggregates – agglomerates), in other words, existence of intermediate structural units between atomic/molecular and macroscopic levels, usually call hierarchical structures. The combined USANS/SANS is one of the best techniques using at present time for characterization of the hierarchical structures, which in many cases shows fractal behavior. The current presentation is focused at the mass and surface fractals discovered experimentally in the sedimentary rocks, attractive colloidal glasses and aggregates of soot particles in MCT-30 engine oil. Some of the fractal structures, particularly the surface fractals in rocks, are extended over three orders of magnitude in the length scale; therefore, application of the combine USANS/SANS technique, which covers the Q-range extended over five orders of magnitude in the reciprocal space ( $2 \times 10^{-5} \text{ \AA}^{-1} < Q < 1 \text{ \AA}^{-1}$ ), is required to obtain complete structural information for complicated hierarchical structures with fractals.

4:20pm **NT+AS-WeA8 Interaction of Alzheimer's Disease Tau Protein with Model Lipid Membranes**, E.M. Jones, Univ. of New Mexico, M. Dubey, Los Alamos National Lab, P.J. Camp, B.C. Givler, Univ. of New Mexico, J. Biernat, E. Mandelkow, Max Planck Unit for Structural Biology, Germany, J. Majewski, Los Alamos National Lab, E.Y. Chi, Univ. of New Mexico

INVITED

In addition to amyloid plaques, tau neurofibrillary tangles comprise another pathological hallmark of Alzheimer's disease (AD). The mechanism of tau's misfolding and aggregation is unknown, but evidence suggests that tau in AD brains may abnormally interact with the neuronal cell membrane. Using lipid monolayers at the air/water interface and supported lipid bilayers as model membrane systems, we characterized the interaction between 4 tau constructs with membranes of different lipid compositions and elucidated the structure of the protein-membrane films using a combination of biophysical techniques, including pressure-area isotherms, fluorescence microscopy, and x-ray and neutron scattering. Our data show that the full length human tau (hTau40) and its constructs are highly surface active and exhibited strong association with negative DMPG lipids and induced morphological changes observed with fluorescence microscopy, while exhibiting weaker and no interactions with positive DMTAP and neutral DMPC lipids. To elucidate molecular-scale structural details, we used X-ray scattering techniques to study tau and lipid monolayer association. X-ray

reflectivity modeling indicated hTau40's presence under a DMPG monolayer and partial insertion into the lipid headgroup region, while grazing incidence X-ray diffraction data showed hTau40 insertion disrupted lipid packing. We also used neutron reflectivity assays to investigate hTau40's ability to disrupt lipid bilayers. The protein completely disrupted a DMPG bilayer while not affecting a neutral DPPC bilayer. These results indicate hTau40 has a propensity to interact with a negatively charged membrane surface and disrupt lipid packing, suggesting a possible protein-aggregate induced mechanism for aggregation and toxicity.

5:00pm **NT+AS-WeA10 Stabilization of a Lipid Multilayer System by Polysaccharides**, M. Kreuzer, M. Strobl, University of Heidelberg, Germany, M. Reinhardt, R. Steitz, Helmholtz-Zentrum Berlin für Materialien und Energie, Germany, R. Dahint, University of Heidelberg, Germany

Hyaluronic acid (HA) is a high molecular weight polysaccharide. It is involved in a wide range of processes in the human body, such as wound healing, tumor progression and joint lubrication. Here we show that HA also stabilizes a lipid multilayer system at physiological conditions. The observed effect may be an important contribution to joint lubrication as lipid films covering the cartilage of natural joints are assumed to reduce internal friction. Neutron reflectometry investigations were carried out at V6 and the new BioRef neutron reflectometer at Helmholtz-Zentrum Berlin. Measurements against excess D<sub>2</sub>O verified, that an oligolamellar DMPC lipid bilayer coating remains stable on a silicon substrate at 21 °C in its ordered state ( $L_{\beta}$ ,  $P_{\beta}$ ) with a d-spacing of 66 Å, but detaches almost completely from the solid support at 38 °C in its chain-disordered state ( $L_{\alpha}$ ). By contrast, oligolamellar lipid bilayers remain stable on a substrate at 38 °C when incubated with a solution of HA in D<sub>2</sub>O. Lamella transformations occur over time, resulting in a new lamella phase with a d-spacing of 233 Å. This effect has to our knowledge not been reported before on solid-supported oligolamellar systems. We will discuss potential consequences of the "new" lamella phase with respect to further insight into joint lubrication.

5:20pm **NT+AS-WeA11 Neutron Reflectometry, QCM-D, and TIRF Study of the Interaction of Endoglucanases with Films of Amorphous Cellulose**, M. Kent, Sandia National Laboratories

INVITED

Cellulase enzyme cocktails include exoglucanases that digest cellulose chain ends and endoglucanases that cleave randomly at interior points along the chains. While it is known that these enzymes work synergistically, the details are not fully understood. In addition, cellulose binding domains (CBDs) are known to play an important role in the digestion of crystalline cellulose but much less is known about the benefit of CBDs in the digestion of amorphous cellulose. Amorphous cellulose is of interest as pretreatment of biomass with ionic liquids, a promising next generation technology, results in a combination of amorphous cellulose and cellulose II. Determining the full effects of endoglucanase activity is challenging because these enzymes can alter the structure of insoluble cellulose in addition to releasing soluble oligomers. To unravel the actions of endoglucanases and the role of cellulose binding domains in enhancing activity on amorphous cellulose, we have combined studies of the profile of water through cellulose films during digestion by neutron reflectivity, measurements of changes in mass and film stiffness using a quartz crystal microbalance (QCM), and visualization of the motion of individual enzymes by total internal reflection fluorescence (TIRF) microscopy.

# Thursday Morning, November 3, 2011

## Applied Surface Science Division

Room: 102 - Session AS-ThM

### Analysis of Insulators and Challenging Samples

**Moderator:** D.J. Gaspar, Pacific Northwest National Laboratory

8:00am **AS-ThM1 Imaging and Differentiation of Epicuticular Waxes on *Arabidopsis thaliana* Organs by TOF-SIMS**, *G.L. Fisher*, Physical Electronics, *P. Wong, C. Buschhaus, R. Jetter*, University of British Columbia, Canada

TOF-SIMS has emerged as an important tool for imaging mass spectrometry of biological samples due to its unique capability to detect molecular ion fragments and elemental ions at sub-micron spatial resolution and without the sample treatments required by e.g. the MALDI technique. For many biological specimens, the ability to image samples having a large degree of surface topography is also highly desired. The resulting elemental and molecular images provide important information regarding the composition of biointerfaces, for example between plant tissues and their natural environment. This TOF-SIMS study involves the differentiation and characterization of epicuticular waxes present at the surfaces of *Arabidopsis thaliana* organs including the flower, stem, adaxial (top) leaf surface and the abaxial (bottom) leaf surface.

High spatial resolution images obtained from a flower petal, an adaxial leaf surface, and an abaxial leaf surface revealing spores, trichomes and respiratory pores, respectively, demonstrate the capability of TOF-SIMS to image molecular ion fragments with a spatial resolution of < 0.3 microns. Total ion images, and molecular fragment ion images of epicuticular wax components, demonstrate the capability to image entire organ surfaces without topographical artifacts. High mass range spectra in both the positive and negative secondary ion polarities reveal that the epicuticular surface of each *Arabidopsis thaliana* organ is comprised of distinct wax components. Mass spectra acquired from specialized cells forming the 1  $\mu\text{m}$  x 7  $\mu\text{m}$  respiratory pores of the abaxial leaf surface indicate that, even within a single organ surface, the epicuticular wax composition may vary. The differences in wax composition on each of the interrogated organs of *Arabidopsis thaliana* will be presented and discussed. Structural assignments for characteristic mass spectrometric features related to the wax composition will also be presented and discussed.

8:20am **AS-ThM2 Aqueous SIMS – Towards in Situ Detection of Chemical Reaction Intermediates in Aqueous Solutions**, *Z. Zhu, L. Yang, X. Yu, M.J. Iedema, J.P. Cowin*, Pacific Northwest National Laboratory

This research provides the first in-situ detection of aqueous surfaces using time-of-flight secondary ion mass spectrometry (ToF-SIMS). ToF-SIMS provides a molecular recognition capability with super-low detection limits, making it a great choice to detect short-lifetime chemical reaction intermediates in aqueous solutions. However, it is difficult to detect aqueous solutions by ToF-SIMS because ToF-SIMS is a high vacuum technique, and the vapor pressure of water is about 2-3 kPa at room temperature. We designed and fabricated a self-contained microfluidic module, allowing in-situ analysis of aqueous surfaces by ToF-SIMS. Microfluidic channels were prepared on top of a block of polydimethylsiloxane (PDMS) using a patterned silicon template with soft lithography techniques, and then a ~100nm thick silicon nitride film was placed on top of the microfluidic channels, on which a small hole with a diameter of ~2-3 microns could be drilled using a focused primary ion beam in a ToF-SIMS instrument. De-ionized water, heavy water, a 0.5% (weight ratio) formic acid aqueous solution, a 0.5% glycerol aqueous solution, and a 0.5% glutamic acid aqueous solution were successfully analyzed through the small hole using our ToF-SIMS instrument (IONTOF-V). The pressure in the analysis chamber was usually at ~5E-7 mbar during measurements, and this value was sufficient for ToF-SIMS analysis. Our device could be safely staying in vacuum for more than 8 hours, and 1 hour continuous SIMS measurements were practical. Molecular signals (M-H) from formic acid (HCO<sub>2</sub><sup>-</sup>), glycerol (C<sub>3</sub>H<sub>7</sub>O<sub>3</sub><sup>-</sup>), and glutamic acid (C<sub>5</sub>H<sub>8</sub>NO<sub>4</sub><sup>-</sup>) were clearly observed in the small hole, but not elsewhere. Based on current data, the detection limits of formic acid, glycerol, and glutamic acid were estimated to be <0.01% (weight ratio).

8:40am **AS-ThM3 Challenges of the XPS Analysis of the Ionic Liquid [BMIM][PF<sub>6</sub>]**, *R.R. Harl, B.D. Booth, G.K. Jennings, B.R. Rogers*, Vanderbilt University

Room temperature ionic liquids (ILs) are ionic compounds that are liquids at ambient conditions due to a bulky, asymmetric organic ion that inhibits crystalline packing. The inhibition of crystalline packing results in ILs having a vapor pressure that is negligibly low. The properties of ILs make them candidates for applications such as nonvolatile solvents, electrolytes, and lubricants. The ionic liquid pair 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>] is being investigated for use as a lubricant in micro-electrical mechanical systems (MEMS). Surface properties are important in tribological applications like lubrication and the negligible vapor pressure of the [BMIM][PF<sub>6</sub>] ionic liquid makes it compatible with traditional surface analysis tools like x-ray photoelectron spectroscopy (XPS).

XPS analysis of ILs is challenging due to the ability of the ionic molecules within the ILs to freely move within the sample. Also, since the ILs are comprised of charged molecules, the motion of the molecules and their relative position within the sample may be affected by changes in surface charging brought about by photoelectron emission or by the electron and ion beams used to neutralize surface charging.

We will present results of our XPS analyses of [BMIM][PF<sub>6</sub>] ionic liquid drop-cast onto a silicon substrate. We dropped enough of the IL to form an approximately 150 nm thick film to mimic a film that would be used for lubricating a MEMS device. However, the IL drop-cast in this manner did not form a continuous film, but rather beaded up on the silicon substrate. Under certain analysis conditions we can force the IL droplets to coalesce into a continuous film.

Preliminary results show that when the surface is positively charged the PF<sub>6</sub> molecule segregates to the liquid/vacuum interface. This observation is consistent with previous studies. When the IL surface is negatively charged the C1s peak shape changes from that indicative of the imidazole ring C-N bonding to that indicative of C-C bonding, most likely from the butyl chains of the BMIM molecules. This change in the C1s spectrum suggests the BMIM molecules are segregating to the liquid/vacuum interface. A corresponding drop in the F1s peak intensity suggests that the PF<sub>6</sub> molecules are moving deeper into the sample.

Along with the XPS results we will propose a mechanism by which the charge and/or energy provided by the x-ray, electron and ion beams induce the change from dispersed droplets to a continuous film. We will also provide insight into how these results could be used in developing or using ILs for MEMS lubricants.

9:00am **AS-ThM4 Working with Difficult Samples - Preparation, Damage, Charging and Data Analysis**, *D.R. Baer, M.H. Engelhard, A.S. Lea, P. Nachimuthu, Z. Zhu*, Pacific Northwest National Laboratory  
**INVITED**

X-ray Photoelectron Spectroscopy (XPS) and other surface analysis methods (e.g. AES and SIMS) are playing increasingly important roles in the analysis of many materials ranging from ancient artifacts, geological minerals and even biological specimens to modern very complex nanostructured materials. Samples that need to be analyzed can be made up of components with a wide variety of physical and chemical properties that impact how they can be handled, prepared, mounted and analyzed without destroying the information that is sought from the analysis. During this presentation a variety of the methods and approaches needed to characterize a range of sample and analysis challenges that we have faced in the EMSL, a US Department of Energy user facility, will be discussed. Analysis challenges discussed will include: inexperienced users and their expectations; sample handling, preparation (including extraction of particles from aqueous solution) and mounting (including anaerobic transfer and freezing); identifying and dealing with damage; identifying and controlling impacts of charging (which are not always obvious); and analysis approaches used to extract information about the nanostructure of complex materials. The materials and materials systems to be discussed will include the impact of processing on catalyst surface composition and chemistry, the oxidation state of species adsorbed on mineral surfaces, the nature and properties of organic layers on inorganic substrates, and the nature of the surfaces and intentional as well as inadvertent coatings (shells) on nanoparticles. Some of the methodology and special capabilities developed in EMSL for controlling sample environments, the value of more rapid and enhanced data analysis, and the importance of procedural guides and standards will be noted. Although many of the topics discussed relate to a variety of surface analysis and other methods, the talk will focus on XPS and use TOF-SIMS to provide an example of challenges associated with

measurement of hydrogen. The importance of complementary measurements by a variety of methods (including XRD, TEM, APT, SEM and RBS) will be highlighted.

Aspects of the work have been supported by the Offices of Basic Energy Sciences and Biological and Environmental Research of the US DOE and by the National Institute of Environmental Health Science under grant NIH U19 ES019544. Portions of this work were conducted in the Environmental Molecular Sciences Laboratory (EMSL), a DOE user facility operated by Pacific Northwest National Laboratory for the Office of Biological and Environmental Research of the DOE.

10:40am **AS-ThM9 Transient Electron Emission from Insulators under Pulsed Electron Beam Injection**, *Y. Kimura, H. Koyama, H. Makino, H. Shinada*, Hitachi, Ltd., Japan, *Y. Mochizuki, H. Kazumi*, Hitachi High-Technologies Corp., Japan

Electron emissions from poorly conductive specimen stimulated by photon and electron injections result in charging phenomena. These can cause distortion of data in electron spectroscopy and image artifacts in scanning electron microscopy because surface potential which influence the motion of emitted electron is modified by charging and change time dependently. Therefore, time dependence of electron emission yields are important for understanding of radiation induced charging of resistive materials.

In this study, we present the transient characteristics of electron emission from SiO<sub>2</sub> using a new experimental facility (Pulsed Electron Microscope: PULSEM) built in the present work. Main feature of the PULSEM, as with electron beam testing system, is a beam blanking system attached below the condenser lens. The beam blanking pulses electron beam into the minimum number of 6 electrons under the condition of primary beam current  $I_p = 20$  pA and beam-pulse-width  $t_p = 50$  ns. The Everhart-Thornley detector with high response scintillator, afterglow time of which is 0.5 ns, and with a photomultiplier is synchronized to the beam blanking system. Transient SE signal as a function of the number of injected electrons is obtained.

Time-dependent electron emission yield ( $\sigma$ ) with the resolution of 30 ns is investigated as a function of the primary electron dose which is controlled by pulse duration ( $\Delta t$ ) as well as primary energy ( $E_p$ ). Quasi static emission yield, which assumed to be intrinsic electron emission in the absence of charging, is obtained under low dose condition of below 60 electrons with  $I_p = 20$  pA and  $\Delta t = 500$  ns. The maximum yield ( $\sigma_m$ ) and its corresponding energy ( $E_m$ ) are 2.5 and 300 eV, respectively. With the increase in electron dose,  $\sigma$  approaches unity due to a charging effect. Finally, we will present total electron emission yield curves in the range of  $E_p < 6$  keV and  $50$  ns  $< \Delta t < 500$  ms.

11:00am **AS-ThM10 High Resolution XPS Chemical State Imaging of Fuel Cell Membranes**, *S.N. Raman, P.E. Larson, J. Moulder, J.S. Hammond*, *S. Alnabulsi*, Physical Electronics USA

Nafion based membranes are being developed for applications in fuel cells. These fuel cell membranes are multi-layer structures with a permeation membrane and two thin layers of noble metal in a polymer matrix acting as the anode and the cathode of the fuel cell. The cross-sectional chemical analysis of these membranes, both new and used, may be extremely useful in improving the performance of the fuel cells. In this study we will highlight new and advanced scanning XPS microprobe based techniques to provide cross-sectional line scans and high resolution chemical mapping of these membranes. The line scan and chemical mapping results elucidate the modifications of the membrane chemistry as a function of use.

11:20am **AS-ThM11 Gas-Cluster Ion Beam Secondary Ion Mass Spectrometry Characterization of Thin Films for Organic Electronics Applications**, *D.J. Gaspar*, Pacific Northwest National Laboratory, *S.R. Bryan*, Physical Electronics USA, *T. Miyayama*, ULVAC-PHI, Japan, *A.B. Padmaperuma, J.S. Swensen, E. Polikarpov*, Pacific Northwest National Laboratory

Organic light emitting devices (OLEDs) have the potential to dramatically change the way we light our living spaces. OLEDs offer the potential for high efficiency lighting from a large area source, with the possibility of transparent and flexible lighting as well. Currently, OLED displays are found commercially in cell phones and in televisions in limited production. One of the key barriers holding back widespread adoption of OLEDs for both lighting and other products is the challenge of generating long-lived devices, particularly for high-efficiency phosphorescent blue OLEDs (a necessary component of high-efficiency white OLEDs). Challenges in the design of stable materials are hampered by our relatively poor ability to measure degradation products in situ, or in ways that ensure we have not damaged the material in the measurement process. To this end, we have generated thin films of single blue phosphorescent OLED components, multilayer films, and working OLEDs before and after aging. These components including the well-studied bis[2-(4,6-difluorophenyl)pyridyl-N,C2']iridium (III) (FIrpic), 2,8-bis(diphenylphosphoryl)dibenzothiophene

(PO15), 4-(diphenylphosphoryl)-N,N-diphenylaniline (HM-A1) and di-[4-(N,N-ditoly-amino)-phenyl]cyclohexane (TAPC). Based on previous experiments in our lab and literature reports, FIrpic and PO15 are known to undergo degradation reactions under conditions similar to those used in this series of experiments. Analysis of these films and systems by gas cluster ion beam secondary ion mass spectrometry (GCIB-SIMS) and other methods show degradation products, which permit the development of useful models for their degradation pathways. These results clearly demonstrate the utility of GCIB-SIMS in the characterization and analysis of OLED devices and materials, and should enable better design and screening of stable materials for high-efficiency OLEDs.

**Biomaterial Interfaces Division**  
**Room: 108 - Session BI-ThM**

**Biomedical Materials**

**Moderator:** S.L. McArthur, Swinburne University of Technology, Australia

8:20am **BI-ThM2 Surface Characterization: A Critical Component in Understanding the Biocompatibility of Biomaterials**, *L. Salvati, S. Vass, DePuy Orthopaedics* **INVITED**

A biomaterial is defined as "any synthetic material or device—e.g. implant or prosthesis—intended to treat, enhance or replace an aging or malfunctioning native tissue, organ or function in the body" David Williams, states that "**Biocompatibility is largely about the chemical interactions that take place between the materials and the body fluids, and the physiological responses to these reactions.**" These reactions are dominated by the initial events at the molecular level, the interface, thus it is not hard to see the relationship between the implant surface properties and it's in vivo. It is clear that the performance of a biomaterial is directly linked to the surface chemistry, composition and topography of the device. However, despite the preponderance of evidence, biomedical device companies as a whole do not utilize surface analytical methods nearly enough. Why is that?

In orthopaedics, most of the implants are fabricated from metals which directly contact biological fluids that are typically complex aqueous mixtures. Consequently corrosion and/or corrosion prevention are important considerations in device manufacturing. For the most part, orthopaedics manufacturers utilize the same passivation methodologies used to impart corrosion resistance to stainless materials. Numerous researchers have characterized the impact of acid passivation on stainless materials, but little has been done to study the effect of these treatments on the CoCr alloys. One of the topics in this presentation deals with the effects of passivation on CoCr alloys. Specifically, the presentation will correlate specific surface treatments with surface chemistry and ultimately to metal ion release. The study will also address questions relating to the use of Citric acid as a green replacement for nitric acid passivation. There is no argument that the process is much greener, but there are plenty of questions as to its effectiveness. Considering that the "changes" imparted by the passivation solutions effect the outer most 10-100Å, the only means to characterize the affects of passivation requires surface analysis methodologies. The importance of surface analysis methods, especially XPS, will be highlighted by this example.

In addition to the discussion of metal alloy passivation, this presentation will also deal with other surface related issues that could impact the biocompatibility of biomaterials. The talk will show the potential impact of packaging materials and cleaning processes on the surface chemistry and composition of biomaterials.

9:00am **BI-ThM4 XPS Sputter Depth Profiling of Organic Materials Using a Coronene Ion Source**, *S.J. Hutton, C.J. Blomfield, A.J. Roberts, S.C. Page, S.J. Coultas*, Kratos Analytical Ltd, UK, *C.E. Moffitt, D.J. Surman*, Kratos Analytical Inc

Controlled release of active pharmaceutical molecules from biocompatible polymers over defined time periods is an area of intense study. Present applications include drug eluting stents and other drug delivery systems. One of the most important parameters which govern drug dosing is the drug concentration depth profile in the supporting polymer matrix. In a previous study we have shown that combining X-ray photoelectron spectroscopy (XPS) with a coronene ion source is a very powerful tool for investigating the drug distribution with depth of a model system [1].

The use of cluster ion sources for sputter depth profiling of thin film or multilayer organic materials during XPS analysis has become routine. A wide range of organic systems are amenable to profiling and there is a good understanding of the experimental parameters which contribute to successful analysis. Here we report on extending the aforementioned study

to materials which closely resemble real world samples intended for use in vivo.

[1] A. Rafati, M.C. Davies, A.G. Shard, S. Hutton, G. Mishra, M.R. Alexander, *J. Controlled Release*, **2009**, *138*, 40–44

9:40am **BI-ThM6 Amino-rich Plasma Polymer Films Prepared by RF Magnetron Sputtering**, *J. Hanuš, G. Ceccone, F.J. Rossi*, European Commission, JRC. Institute for Health and Consumer Protection, Italy  
RF magnetron sputtering of nylon 6.6 was used for the deposition of nitrogen rich films. Deposition was followed by N<sub>2</sub> H<sub>2</sub> plasma post-treatment to enhance primary amine concentration on the surface. Maximal reached NH<sub>2</sub> concentration was 11 % with aminoselectivity 13.5 %. The films exhibited small negative z-potential at basic pH with isoelectric point ~ pH 4.5. Bio properties of the films were tested by QCM in terms of ability to adsorb different proteins and their antigens. The interaction between the film and the buffer solution was also studied and compared to other films such as poly-acrylic acid and PEO plasma polymers. The results show that these films are stable and can be used as a platform where positively charged surfaces are needed

10:40am **BI-ThM9 Surface Analysis in Biotech & Pharma: A Surfeit of Frontiers**, *E. Johnston*, Genzyme **INVITED**

Surface and interfacial analytical tools continue to provide new value and find unexpected new uses in the biotech and medical device industries. Some uses are investigational in nature and help solve critical problems within manufacturing and quality control. Other applications fall squarely within the realm of R&D - tilting the balance between feasibility of a product or obsolescence of a project, or providing fresh insight into the nature of biomaterial/biological interactions. By way of example, a study will be presented illustrating how TOF-SIMS was used to image a phosphate-binding drug particle in the complex matrix of the rat gastrointestinal tract. Sample preparation was challenging due to the highly hydrated nature of the tissue material. The results yielded surprising information about the ions that bind to this cationically charged particle and opened new avenues for inquiry and study.

11:20am **BI-ThM11 Enhancing Monoclonal Antibody Drug Detection by Developing a Microparticle-based Immunoassay**, *N. Mendez, M.E. Ruidiaz, A.B. Sanchez, B.T. Messmer, A.C. Kummel*, University of California San Diego

Monoclonal antibodies are a notable and rising class of cancer therapeutics due to their enhanced targeting and immune system stimulation properties. Dosage guidelines are typically developed with many uncertainties which may affect treatment outcome and cause unwanted side effects. The requirement for an assay that can quickly and precisely measure the concentration of the monoclonal antibody in a serum sample of a patient during therapy is needed. The present study has demonstrated that the key to detection is compensation for variation in non-specific binding of serum to the assay surface. A microparticle-based assay with peptide antigen mimetics has been developed to rapidly determine the concentration of antibody drug present in serum specimens with high sensitivity. Alemtuzumab (anti-CD52) and rituximab (anti-CD20) antigen peptides, as discovered by phage display, were synthesized on 10 µm TentaGel resin beads using conventional solid phase peptide synthesis techniques. The microparticle beads were modified to allow for multiplexing and microfluidic handling via fluorescent labeling and magnetic functionalization. The antigen-displaying fluoromagnetic particles were incubated with spiked serum samples which allowed free antibody to be captured. Primary antibody detection was performed on alemtuzumab while rituximab detection was used to compensate for non-specific serum binding to the beads. After washing, the beads were incubated with a fluorescently tagged secondary antibody for detection by flow cytometry. Serum from thirty (30) individual donors with various spiked serum concentrations of antibody drug were assessed using this assay. Analysis of bead fluorescence data allows for a limit of quantitation down to 0.5µg/ml of serum antibody drug concentration. Using detection of an antibody known to be absent in serum, an accurate compensation technique for non-specific binding has been developed on multifunctional antibody assay beads in realistic samples. The developed assay is robust against donor serum variation.

11:40am **BI-ThM12 Controlling the Hydroaffinity of Silicone/Hydrophobic Acrylic Surfaces of Intraocular Lenses using Visco-Elastic Colloids and Blood Proteins**, *N.X. Herbots, ASU / SiO2 NanoTech Inc. / SiO2 Associates, LLC, R.J. Culbertson, Q.X. Bradley, D.A. Sell, A.M. Murphy*, Arizona State U., *C.H. Sell*, Arizona Vitro-Retinal Consultants, *H.M. Kwong*, Arizona Vitro-Retinal Consultants / ASU, *T. Kutz, A.S. Benitez, M.A. Hart, B.J. Wilkens, R.B. Bennett-Kennett*, Arizona State U.

Over 15 million cataract surgeries are performed each year world wide. 2-6 % of cataract patients suffer subsequently from diabetic and other retinal issues post surgery due to aging and accidents and must undergo a secondary eye surgery. Secondary surgery performed after implantation of artificial intra-ocular lenses (IOLs) can fail due to the fogging of IOLs from condensation of bodily fluids. New, high performance accommodating silicone and hydrophobic acrylic IOLs can fog during such surgery. This work solves the problem by modifying water affinity of IOLs using a polymer emulsion, VitreOx™ [1-5] with a 100% success rate in the lab. Ten clinical trials yielded a success rate of 80% in the year 2010-211 with failure inferred to be due to blood proteins on IOLs.

Thus, the role of hydro-affinity of blood proteins preventing coagulation, heparin, present during surgery, has to be investigated. Our results show that heparin behaves identically to H<sub>2</sub>O on hydrophobic surfaces. Heparin simply de-wets on silicone IOLs and hydrophobic acrylic lenses. It does not prevent fogging on IOLs nor interfere with our anti-fogging emulsion.

Fibrinogen is the other protein investigated because it enhances blood coagulation and is often present in trauma situations. Fibrinogen applied to IOLs in various dilutions does prevent fogging. However, it cannot be removed after application on the IOLs, thus remaining as a potent coagulant agent in the eye. Thus fibrinogen can indeed prevent fogging, but is not viable since it cannot be removed after application like VitreOx™. Fibrinogen could explain why some IOLs fog while others do not during emergency secondary eye surgery.

[1] U. S. Patent Application "Molecular Films for Hydrophobic Implant Surfaces" N. Herbots, J. D. Bradley, M.A. Hart, D.A. Sell, S. D. Whaley, Q. Xing Bradley Filed 11/9/10

[2] "Modeling Mechanisms of Water Affinity & Condensation on Si-based Surfaces via Experiments & Applications" by Q. Xing, ASU (2011).

[3] N. Herbots, Q. Xing, M. Hart, J. D. Bradley, D. A. Sell, R. J. Culbertson, B. J. Wilkens; "IBMM of OH Adsorbates and Interphases on Si-based Materials" Nucl. Instr. & Meth. B, IBMM 17 (2010), accepted.

[4] Q. Xing, M. A. Hart, R. J. Culbertson, J. D. Bradley, N. Herbots, B. J. Wilkens, D. A. Sell, C. F. Watson; "Particle-Induced X-ray Emission of Silicate Coatings on High Impact Resistance Polycarbonates". 21st ICAARI (2010), accepted

[5] Q. Xing, N. Herbots, M. Hart, J. D. Bradley, B. J. Wilkens, D. A. Sell, C. H. Sell, H. M. Kwong, R. J. Culbertson, S. D. Whaley; "Ion Beam Analysis of Silicon-Based Surfaces and Correlation with Surface Energy Measurements?". 21st ICAARI (2010), accepted.

## Spectroscopic Ellipsometry Focus Topic

**Room: 209 - Session EL+AS+EM+MS+PS+TF-ThM**

### Spectroscopic Ellipsometry of Biological Materials and Organic Films

**Moderator:** M. Creatore, Eindhoven University of Technology, the Netherlands, K.G. Lloyd, DuPont Corporate Center for Analytical Sciences

8:00am **EL+AS+EM+MS+PS+TF-ThM1 Application of Various Spectroscopic Ellipsometry Techniques for In Situ Studies of Thin Polymer Films on Solid Substrates**, *K.-J. Eichhorn*, Leibniz-Institut für Polymerforschung Dresden e.V., Germany **INVITED**

Thin films of functional polymers are not only widely integrated into modern micro- and nanoelectronic devices, but also used to modify solid surfaces for biosensor, biomedical and antifouling applications.

Therefore, in the first part I will report on improved temperature-dependent spectroscopic Vis-ellipsometry experiments to study confinement effects on the polymer dynamics in thin films to address a question which is controversially discussed in the polymer physics community for a long time past: Is there really a significant change of the glass transition temperature T<sub>g</sub> of polymers when confined in nanoscopic films (studied here down to about 10 nm thickness)? We compared well-known linear polystyrenes of different molecular weights /1/ and hyperbranched polyesters having

different architectures and functional groups [2]. Films of different thickness were prepared by spin-coating on silicon wafers, carefully equilibrated and measured in dependence on temperature (up to 250°C) in an inert gas atmosphere. The T<sub>g</sub> data were determined from the ellipsometric results and discussed.

In the second part, “smart” surfaces will be presented which can be used for controlled adsorption and release of biomolecules. For that, different types of stimuli-responsive polymer brushes were prepared on solid substrates by a “grafting-to” procedure. The brush properties (e.g. swelling/collapsing) as well as the resulting adsorption/desorption of model proteins (e.g. Human Serum Albumin, Chymotrypsin) can be switched in an appropriate aqueous medium with temperature (PNiPAAm) and/or pH (PAA-P2VP). The corresponding processes at the solid-liquid interface were studied in-situ by spectroscopic Vis- and IR-ellipsometry [3,4].

/1/ M. Tress, M. Erber, E.U. Mapeša, H. Huth, J. Müller, A. Sergei, C. Schick, K.-J. Eichhorn, B. Voit, F. Kremer, *Macromolecules* 43 (2010), 9937-9944

/2/ M. Erber, A. Khalayavina, K.-J. Eichhorn, B. Voit, *Polymer* 51 (2010), 129-135

/3/ E. Bittrich, M. Kuntzsch, K.-J. Eichhorn, P. Uhlmann, *J. Polym. Sci. B, Polym. Phys.* 48 (2010), 1606-1615

/4/ Y. Mikhailova, L. Ionov, J. Rappich, M. Gensch, N. Esser, S. Minko, K.-J. Eichhorn, M. Stamm, K. Hinrichs, *Anal. Chem.* 79 (2007) 20, 7676-7682

**8:40am EL+AS+EM+MS+PS+TF-ThM3 Hard Matter Meets Thin Polymer Films-Spectroscopic Ellipsometry as a Versatile Tool to Investigate Properties of Responsive Poly(N-isopropylacrylamide) Systems with Incorporated Magnetic Nanoparticles.** S. Rauch, Leibniz-Institut für Polymerforschung Dresden e. V., Germany

Responsive polymer systems designed by using polymer brushes or hydrogels are interesting systems, which can exhibit reversible or irreversible changes in their physical and structural properties to special environmental conditions (e.g. temperature or magnetic fields). The temperature responsive poly(N-isopropylacrylamide) (PNiPAAm) is one of such polymers. It undergoes a phase transition in aqueous solution at its lower critical solution temperature (LCST) of 32 °C which induces an increase in hydrophobicity. Combined with the properties of magnetic nanoparticles (NP) (e.g. Fe<sub>3</sub>O<sub>4</sub> or CoFe<sub>2</sub>O<sub>4</sub>) these systems can lead to new surface functionalities with new interesting properties for many applications, as sensing, wettability or (bio)adhesion.

For the design of such thin film systems a basic knowledge of the film characteristics is essential. Therefore it is first necessary to know how much nanoparticles are inside or attached to the system. By using spectroscopic Vis-Ellipsometry (SE) it is not only possible to investigate optical properties of these films but also the composition of it, e.g. volume fraction of Fe<sub>3</sub>O<sub>4</sub>-NP.

We studied two types of films and present results for a thin NP-composite film prepared by pre-mixing of the PNiPAAm with hydrophobic Fe<sub>3</sub>O<sub>4</sub>-NP, spin-coated and grafted to a silicon substrate (System 1) and a film prepared by adsorption of hydrophilic functionalized Fe<sub>3</sub>O<sub>4</sub>-NP onto PNiPAAm brushes (System 2). The former system was chosen to develop an optical model starting from a simple two component effective-medium-approach (Maxwell-Garnett-EMA) using the optical constants of the pure polymer measured by SE and of Fe<sub>3</sub>O<sub>4</sub> with averaged data taken from three different publications. The SE best fit-results were validated against scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS).

After transferring this optical model to System 2, the adsorption of hydrophilic functionalized Fe<sub>3</sub>O<sub>4</sub>-NP onto PNiPAAm brushes was investigated and will be discussed with additional results obtained from contact angle (CA) and phase transition (LCST) measurements.

**9:00am EL+AS+EM+MS+PS+TF-ThM4 The White Scarab Beetle *Cyphochilus insulanus* –Scattering and Polarization Properties.** C. Akerlind, Swedish Defence Research Agency / Linköping University, Sweden, H. Arwin, Linköping University, Sweden, T. Hallberg, H. Kariis, Swedish Defence Research Agency, Sweden, J. Landin, K. Järrendahl, Linköping University, Sweden

Three methods were used to characterize the optical properties of the light scattering white scarab beetle *Cyphochilus insulanus*. Spectral directional hemispherical (DH) reflectance measurements in the wavelength region 250 nm to 25 µm were performed using integrating spheres. The general spectral appearance shows a relatively strong reflectance band in the range 400 - 1600 nm. The Bidirectional Reflection Distribution Function (BRDF) was measured over a semi-circle in the plane of incidence at the wavelengths 633 nm and 3.39 µm, using s- and p-polarized light. In the visible the BRDF data shows a near Lambertian behaviour with a constant

BRDF for most angles, i.e. the light is diffusely scattered. For large incident angles and in the infrared the BRDF is more specular. Full Mueller-matrix spectroscopic ellipsometry (MMSE) measurements were performed in the wavelength range 250 - 1000 nm at angles of incidence between 45° and 75° using a dual rotating compensator ellipsometer. The Mueller data show that the reflected light in general has a high degree of polarization *P* even for nonpolarized incident light. The angular dependence of *P* was pronounced for incident p-polarized light and was very low near the Brewster angle. In comparison, *P* was high for all measured angles for incident s-polarized light. Close to the Brewster angle, the reflected light showed a high ellipticity for incident p-polarized light. The optical data is used to model the structure and optical response of the beetle cuticle. With input from the DH and BRDF-data analysis of the Mueller Matrix data was made using Fresnel-based layer modelling. 2-, 3- and n-phase models are compared. The obtained optical properties are also used to calculate color data in terms of chromaticity and whiteness. The scattering properties of the *Cyphochilus insulanus* cuticle are also discussed by combining the BRDF and MMSE data as well as recently obtained Mueller matrix imaging polarimetry results.

**9:20am EL+AS+EM+MS+PS+TF-ThM5 Real-time Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation Characterization of Biomolecule Adsorption within Sculptured Thin Films.** T. Kasputis, D. Schmidt, K.B. Rodenhausen, H. Wang, A.K. Pannier, M. Schubert, University of Nebraska - Lincoln

Recent improvements in nanofabrication strategies have led to the development of precisely crafted nanostructures with intricate features. Incorporating biomolecules such as proteins, DNA, drugs, and even whole cells could allow for functionalization of nanostructured surfaces for biological applications including biosensing, tissue engineering scaffolds, and drug and gene delivery. Along with the nanofabrication of biological devices, there is a need to develop instrumentation capable of probing and characterizing the dynamic evolution of these bio-functionalized interfaces. Spectroscopic ellipsometry combined with quartz crystal microbalance with dissipation (SE/QCM-D) is a non-destructive optical/mechanical characterization technique that reveals dynamic properties, including average film thickness (with sub-angstrom resolution), adsorbed mass, and porosity.

Nanostructures in the form of sculptured thin films (STF) were fabricated by glancing angle deposition via electron beam evaporation of titanium onto gold-coated quartz sensors. The sensors were then mounted within an SE/QCM-D liquid cell, and proteins of varying sizes were deposited and characterized, *in-situ*. Protein adsorption was detected shortly after introducing the protein solutions by SE and QCM-D as a change in the optical response and decrease of vibration frequency, respectively. QCM-D reported greater adsorbed mass for larger proteins (fibronectin) than smaller proteins (bovine serum albumin). The adsorbed mass of proteins within the nanostructured scaffold exceeded that of proteins on flat surfaces, confirming that the STFs are capable of trapping proteins. Analysis of the anisotropic optical response from the nanostructures, which is very sensitive to environmental changes, adds complementary information on protein adsorption; the optical quantification is in agreement with QCM-D results. In addition, the adsorption of other biomolecules, such as cells and DNA complexes, has also been accomplished. The use of combinatorial SE/QCM-D to characterize and monitor the attachment of biomolecules on complex nanotopographies will improve the design and fabrication strategies for a wide array of biotechnological devices.

**9:40am EL+AS+EM+MS+PS+TF-ThM6 Characterization of Multilayer Organic Thin Film for Use as an Aptamer Biosensor with Hybrid Spectroscopic Ellipsometry and Quartz Crystal Microbalance with Dissipation.** J.Y. Gerasimov, K.B. Rodenhausen, H. Wang, R.Y. Lai, M. Schubert, University of Nebraska - Lincoln

DNA aptamer molecules passivated by alkanethiols can be used for biological detection and screening. Through the use of spectroscopic ellipsometry (SE, optical) and quartz crystal microbalance with dissipation (QCM-D, mechanical) techniques, selective binding of analytes to chemisorbed aptamer probes can be observed *in-situ*. The system analyzed consists of a gold-coated quartz substrate, a multilayer organic thin film (containing aptamer probe, alkanethiol, and single-stranded DNA analyte), and physiological buffer solution. The attachment and detachment of material, the hybridization efficiency of the aptamer probes, and changes in the porosity of the multilayer organic thin film were all determined by SE/QCM-D.

In this contribution, we present the real-time SE/QCM-D characterization of (a) the formation of the aptamer probe layer, (b) the subsequent chemisorption of alkanethiol, and (c) the interrogation of single-stranded DNA that is non-complementary or complementary to the sequence found

on the aptamer probe. The aptamer DNA sequence encodes codon 12 of the *K-ras* gene; mutations of this gene are frequently found among pancreatic cancer patients. We found that introduction of either complementary or non-complementary DNA caused increases of the multilayer organic thin film thickness. However, our SE/QCM-D analysis showed that the porosity of the multilayer organic thin film responded differently depending on the compatibility of the DNA analyte. The SE/QCM-D technique provides evidence for different surface attachment mechanisms and can be useful in characterizing biological interfaces.

10:40am **EL+AS+EM+MS+PS+TF-ThM9 Contamination Processes of EUV Optics Characterized by Spectroscopic Ellipsometry**, *L.J. Richter, C. Tarrío, S. Grantham, S.B. Hill, T.B. Lucatorto*, National Institute of Standards and Technology, *N.S. Faradzhev*, University of Virginia

Extreme ultraviolet (EUV) lithography using 13.5 nm light is emerging as a viable tool for semiconductor fabrication at design rules below 32 nm. Tool performance critically depends on limiting and mitigating degradation of the EUV optical elements. A primary degradation mechanism is the EUV induced deposition of carbon from ambient species originating from outgassing of the unbaked vacuum system and/or outgassing from the EUV irradiation of the resist. Using the high brightness of the Synchrotron Ultraviolet Radiation Facility (SURF-III) at NIST both fundamental studies of EUV induced contamination and practical ("witness plate") studies of resist out gassing are performed. Typical deposits are hydrogenated amorphous carbon features with peak thicknesses of about 1 nm and nominal lateral extent of 1 mm. Both *ex-situ*, small spot mapping spectroscopic ellipsometry (SE) and *in situ* single-wavelength imaging nulling-ellipsometry are used for rapid, sensitive, contamination metrology. Fundamental studies of contamination by admitted gases indicate that the process is a complex function of both gas pressure and photon dose. Correlations between SE and XPS are suggestive that, at high EUV fluxes, densification can occur resulting in spatial variation in the deposit dielectric function. The use of principal component analysis of the SE images to highlight the spatial diversity will be discussed.

11:00am **EL+AS+EM+MS+PS+TF-ThM10 Characterization of Organic Solar Cells Materials and Structures by Spectroscopic Ellipsometry**, *J.P. Piel, L. Kitzinger, A. Bondaz, C. Defranoux*, SEMILAB-SOPRALAB, France

Spectroscopic Ellipsometry (S.E) is a well known optical technique widely used for the characterisation of all types of thin films for determination of film thickness and optical indices on glass or plastic substrates.

S.E. is also being applied to the characterization of materials and multilayer structures of organic materials like organic light-emitting diodes (OLEDs) or Organic Solar Cells.

We present the determination of the refractive indices of organic Solar Cells materials like P3HT, PCBM, Pentacene, Perylene, and their blends. Complex organic materials can be analyzed accurately and fully characterized from their absorption bands in the visible and UV range (190nm to 900nm).

Transmission and absorption can be also measured at the same time and be used to determine the optical properties of these materials.

Using these refractive indices, analysis of real multi-layer stacks can be done. The refractive indices can be used afterwards to automatically optimise and balance the energy flow dissipation  $Q$  inside an organic solar cell composed of a thin film stack. We present an example performed on a single cell and on a tandem bi-layer cell structure.

Since these materials are sensitive to moisture and pollution, it can be necessary to measure their optical properties and thickness values through an encapsulated media. We will demonstrate how we can measure single layer properties and multi-layer stacks, through encapsulated samples, from the back side of the substrate. This technique can be applied to test structure or real Organic Solar Cell monitoring. Backside measurement combined with a water vapour cell used for ellipsometry porosimetry is used to test the efficiency of the thin film encapsulation.

We also present the characterization of ITO and ZnO transparent electrodes by S.E. and how near infra-red ellipsometry is used to determine the ITO resistance, without contact, by using the Drude behaviour on encapsulated samples.

## Transparent Conductors and Printable Electronics

### Focus Topic

Room: 106 - Session TC+AS+EM-ThM

### Transparent / Printable Electronics Part 1

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

8:00am **TC+AS+EM-ThM1 Growth Characteristic and Films Properties of Ga doped ZnO (GZO) by Low Temperature Atomic Layer Deposition**, *T.W. Nam, JM. Kim, W.S. Lee, H. Kim*, Yonsei University, Republic of Korea

Atomic layer deposition (ALD) has great benefits over other deposition techniques since its growth mechanism controlled by a self-limited surface reaction exhibits excellent conformality, large area uniformity, and atomic scale thickness controllability. In particular, ALD becomes increasingly more promising thin film deposition method for future flexible electronics. Recently, there have been many research efforts on the investigation of doped ZnO for transparent conducting oxides (TCOs) due to their higher mobility than that of undoped ZnO. Ga doped ZnO (GZO) is one of the promising material for substitution of ZnO. As a representative TCO for applications to the transparent thin film transistor (TTFT) or flexible electronic, GZO thin films by PVD or CVD have been extensively studied. Nevertheless studies on GZO films grown by ALD at low temperature condition which can be applied to flexible devices were still not carried out as far as we know in spite of its potential importance. Hence, for this study, we investigated the growth characteristics and film properties of low temperature ALD (LT-ALD) GZO films by varying deposition method. Field emission scanning electron microscopy (FE-SEM) observation of the GZO films deposited on 5:1 via patterns showed that the film has excellent conformality with over 95 % coverage even at room temperature growth. Additionally, the chemical and microstructural analysis was studied by various analytical techniques including X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and atomic force microscope (AFM). Also spectrophotometer was used to measure a transmittance of the film and showed high transmittance that could be applicable to transparent devices.

8:20am **TC+AS+EM-ThM2 Enhancement of C-Axis Orientation of Ga-doped ZnO Films Deposited on Unintentionally Heated Glass Substrates using Nanosheet Seed Layers**, *H. Makino*, Kochi Univ. of Tech., Japan, *T. Shibata*, NIMS, Japan, *N. Yamamoto*, Kochi Univ. of Tech., Japan, *T. Sasaki*, NIMS, Japan, *T. Yamamoto*, Kochi Univ. of Tech., Japan

Ga-doped ZnO (GZO) film is one of promising candidates as substitute for ITO transparent electrodes in optoelectronic devices. Control of structural properties, especially c-axis orientation, is crucial issue to improve electrical properties of polycrystalline GZO films on glass or plastic substrates [1]. Recently, nanosheet seed layers were proposed to control crystal orientation of oxide films on amorphous substrates [2]. In this study, we employed a seed layer of tungsten oxide nanosheets with two-dimensional hexagonal lattice structure for deposition of GZO thin films on unintentionally heated glass substrates.

The nanosheets were assembled on glass substrates by Langmuir-Blodgett method. The GZO films with thickness of 100 nm were deposited by an ion-plating with direct current arc discharge on unintentionally heated glass substrates with and without the nanosheet seed layers.

The crystal structural properties were characterized by x-ray diffraction measurements. The c-axis orientation of the GZO films was drastically enhanced by the nanosheet seed layers. The intensity of (002) diffraction peak of GZO films deposited with the seed layers was about 40 times as strong as that deposited without the seed layers. The degree of c-axis orientation was evaluated by the (002) x-ray rocking curve (XRC). The full-width half-maximum of XRC of the GZO films on the nanosheet seed layers was  $2.6^\circ$ , which is even lower than that of GZO films deposited on bare glass substrate at  $200^\circ\text{C}$ .

The electrical properties were characterized by Hall effect measurements at room temperature. The GZO films deposited on the nanosheet seed layers showed the resistivity of  $2.9 \times 10^{-4} \Omega\text{cm}$  with the Hall mobility of  $24 \text{ cm}^2/\text{Vs}$  and the carrier concentration of  $9.0 \times 10^{20} \text{ cm}^{-3}$ . On the other hand, the GZO film deposited without the nanosheet seed layers showed the resistivity of  $5.0 \times 10^{-4} \Omega\text{cm}$  with the Hall mobility of  $17 \text{ cm}^2/\text{Vs}$  and the carrier concentration of  $7.2 \times 10^{20} \text{ cm}^{-3}$ . Both the Hall mobility and the carrier concentration were improved by the nanosheet seed layers.

[1] T. Yamada et al., J. Appl. Phys. 107, 123534 (2010). [2] T. Shibata et al., Adv. Mater. 20, 231 (2008).

8:40am **TC+AS+EM-ThM3 Multi-component Transparent Conducting Oxides: Progress in Materials Modeling**, *S.-H. Wei*, National Renewable Energy Laboratory **INVITED**

Transparent conducting oxides (TCOs) play an essential role in modern optoelectronic devices through their combination of electrical conductivity and optical transparency. We review recent progress in our understanding of multi-component TCOs formed from solid solutions of ZnO, In<sub>2</sub>O<sub>3</sub>, Ga<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>, with a particular emphasis on the contributions of materials modeling, primarily based on Density Functional Theory. In particular, we highlight three major results from our work: (i) the fundamental principles governing the crystal structures of multi-component oxide structures including (In<sub>2</sub>O<sub>3</sub>)(ZnO)<sub>n</sub>, named IZO, and (In<sub>2</sub>O<sub>3</sub>)<sub>m</sub>(Ga<sub>2</sub>O<sub>3</sub>)<sub>l</sub>(ZnO)<sub>n</sub>, named IGZO; (ii) the relationship between elemental composition and optical and electrical behavior; (iii) the origin of high-performance of amorphous oxide semiconductors. From these advances, the challenge of the rational design of novel electroceramic materials is discussed.

9:20am **TC+AS+EM-ThM5 Composition Control of Electron Beam Deposited Nb-TiO<sub>2</sub> Thin Films**, *N.A. Beckers, R.T. Tucker*, University of Alberta, Canada, *M.D. Fleischauer*, NRC-National Institute for Nanotechnology, Canada, *M.J. Brett*, University of Alberta, Canada

Nb-doped TiO<sub>2</sub> has been identified as a potential indium-free transparent conductor, and has been fabricated by pulsed laser deposition and sputtering with good success.<sup>1,2</sup> Other deposition methods, such as electron beam evaporation, are of interest for this material but have had limited demonstration to date. It would be advantageous to be able to use electron beam evaporation because in addition to planar films, the collimated flux allows for structured thin films via glancing angle deposition (GLAD). Composition control is essential for doped functional materials, which is typically difficult to obtain through physical mixing of source materials. Here we show that using a sol gel approach to prepare the source materials provides a possible route to circumvent this issue. The facile, solution based sol gel process for the synthesis of ceramic and glassy materials allows for precise composition control by controlling the amounts and ratios of the metal oxide precursors. A sol gel methodology was used to prepare a series of Nb-doped TiO<sub>2</sub> deposition source materials with the following compositions: Nb<sub>0.06</sub>Ti<sub>0.94</sub>O<sub>2</sub>, Nb<sub>0.12</sub>Ti<sub>0.88</sub>O<sub>2</sub>, and Nb<sub>0.24</sub>Ti<sub>0.76</sub>O<sub>2</sub>. We will show that XPS results confirm the composition of the electron beam deposited films and reflects the composition of the source materials. Premixed powders of Nb<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> do not show the same translation of composition as the sol-gel derived source material. Details on the effects of the post-deposition annealing environment on the thin film optical and electrical properties will also be presented.

References:

1. Yamada, N.; Hitosugi, T.; Hoang, N. L. H.; Furubayashi, Y.; Hirose, Y.; Konuma, S.; Shimada, T.; Hasegawa, T. *Thin Solid Films* **2008**, *516*, 5754-5757.
2. Ishida, T.; Okada, M.; Tsuchiya, T.; Murakami, T.; Nakano, M. *Thin Solid Films* **2011**, *519*, 1934-1942.

9:40am **TC+AS+EM-ThM6 Laboratory and Production-Scale Low-Temperature Transparent Conducting Oxide Deposition**, *E. Ritz*, University of Illinois at Urbana Champaign, *G.B. Rayner*, Kurt J. Lesker Company, *D. Andruczyk*, University of Illinois at Urbana Champaign, *T. Dockstader*, Kurt J. Lesker Company, *D.N. Ruzic*, University of Illinois at Urbana Champaign

Transparent conducting oxides (TCOs) are a class of materials that are becoming increasingly ingrained in our daily lives due to their use in electronic displays and mobile devices. There is a strong need to develop an economical deposition technique that allows for high transparency films with high electrical conductivity while replacing costly materials such as Indium Tin Oxide (ITO) with alternatives such as Aluminum-doped Zinc Oxide (AZO). In addition, a low-temperature deposition method would allow creation of TCOs on flexible plastic substrates, such as polyethylene terephthalate (PET). By using a dual DC magnetron system with a secondary RF antenna running at 13.56 MHz, a process has been developed that can deposit TCO films without significantly heating the substrate while maintaining high transmission and electrical properties. This capability has been demonstrated on a small-scale experimental setup utilizing 3-inch diameter circular magnetrons as well as a prototype production-scale chamber operating with 18x3.5 inch rectangular magnetrons aimed at flexible photovoltaic manufacturing. Using an immersed inductive RF antenna, ionization fraction can be increased to over 80%, measured by a gridded energy analyzer, and plasma density increased by an order of magnitude from 10<sup>10</sup> cm<sup>-3</sup> to 10<sup>11</sup> cm<sup>-3</sup>, as measured by Langmuir probe. The secondary plasma deposits energy in the film without heating the substrate above 100°C while still achieving film resistivity on the order of 10<sup>-3</sup>-10<sup>-4</sup> Ohm-cm (measured by four-point probe method) and transparency of greater than 90% in the visible wavelengths (measured by

spectrophotometry.) Adjusting the RF power (0-1000W) and the oxygen content (0-5%) in the plasma enables the ability to tune the film transparency and conductivity to desired levels. Crystal formation of films analyzed by x-ray diffraction (XRD) and elemental composition determined by x-ray photoelectron spectroscopy (XPS).

10:40am **TC+AS+EM-ThM9 Optical and Electronic Properties of Photonic Crystal Based Transparent Conductors**, *S. Narayanan, M. Bockstaller, L. Porter*, Carnegie Mellon University

Transparent conductors are becoming ubiquitous in a host of civil and military applications, including transparent electrical contacts in solar cells and LEDs, heated glass for aircraft and automobile windows, and electrochromic devices and smart windows. However, finding abundant materials with optimal electrical and optical properties and that can be produced economically is a particular challenge. Moreover, limited supply and large demand, of late, for indium has inspired focused research on finding alternatives to ITO as a transparent conductor. We report here a novel approach to control optical properties such as absorption, transmission and reflection in multilayered structures (based on [1-2]) with absorbing components. Appropriate combination of materials could, among others, allow for applications like transparent electrodes, transparent electromagnetic shielding, flexible transparent conductors, etc. Through this study, we have demonstrated the validity of this approach using a few different materials combinations including polymer/metal and metal/ceramic systems. In these realizations the approach was shown to increase the transparency in the visible frequency range by ~ 3 orders of magnitude as compared to the reference materials. For example, transmittances of 30-50% of incident light in the visible region were measured for films containing a polymer (polystyrene - PS) and an amount of metal (gold - Au) that was 3-4 times as thick as its skin depth (~ 40-50 nm). We have also found compatibility between the observed experimental results and numerical simulations. Apart from enhanced optical transmittance, resistivity values of ~ 10<sup>-4</sup> Ωcm (comparable to Au films having ~ 10<sup>-5</sup> Ωcm) have also been discovered in structures having insulating components. Our ongoing and future work is focused on alternative structures to enhance conductivity in the transverse direction as well as incorporate flexibility in the same. **References:** [1] M. Scalora *et al.*, *J. Appl. Phys.* **83** 5 (1998) 2377-2383 [2] M. Scalora, M. J. Bloemer, C. M. Bowden, *Optics and Photonics News* **10** 9 (1999) 24-27

11:00am **TC+AS+EM-ThM10 Effect of Plasma Treatment and Annealing on the Electrical Properties of Spin-Coated Colloidal ITO Films**, *S.M. Joshi, G.W. Book, R.A. Gerhardt*, Georgia Institute of Technology

Colloidal ITO based inks may be an attractive route to direct writing transparent circuits and also be useful for the fabrication of transparent conductive ITO films on complex shaped substrates. The presence of stabilizing ligands and minimal contact between the ITO nanoparticles in the deposited films can be a challenge in obtaining the optimum electrical properties. This study investigates the effect of plasma treatment and annealing on the electrical properties of colloidal ITO films. Crystalline colloidal ITO nanoparticles were synthesized in-house by a non-aqueous technique. The solutions were spin coated onto glass and quartz substrates and their electrical and optical properties were evaluated. All films were found to be completely transparent, while the as-deposited films had resistivities more than 10<sup>8</sup> ohm-cm. Plasma treatments were shown to be effective in removing residual organics in the films, and even without annealing, some recipes were able to reduce the film resistivity by more than four orders of magnitude. Plasma treatments, when done in combination with annealing, resulted in films with resistivities less than 1 ohm-cm.

11:20am **TC+AS+EM-ThM11 Hybrid Organic/Inorganic Materials and Devices for Flexible Electronics Applications**, *M.A. Quevedo-Lopez, J.I. Mejia, A. Salas-Villasenor, A. Carrillo-Castillo, B.E. Gnade*, University of Texas at Dallas, *D. Allee*, Arizona State University **INVITED**

The field of flexible electronics has expanded tremendously over the past few years. Similar to what happened in silicon integrated circuit technology 40 years ago, flexible electronics are now at a point where system design and process integration will drive the technology. Flexible electronics will likely push the limits of material performance, process integration, circuit design, and system integration to demonstrate the full potential of flexible electronics. In general, key components for any flexible electronic application include thin film transistors. In order to be competitive with state-of-the-art a:Si:H thin film transistors, any other thin film transistor technology must show reproducible transistor parameters such as mobility, threshold voltage, drive current and reliability.

A grand challenge in flexible, thin-film-transistor (TFT) circuitry is the development of complementary metal oxide semiconductor (CMOS)



circuits. Although flexible digital circuits, flexible sensors, flexible batteries and solar cells have already been demonstrated, the missing technology piece that must be developed is flexible analog circuitry. For example, an operational amplifier will enable the interface to most sensors and actuators, significantly expanding the functionality of flexible electronic systems. In this paper, we will present n- and p-type chalcogenide-based materials that can be used as the building blocks for analog CMOS-based circuits. In particular, we will introduce the use of chemical bath deposition as an alternative to deposit these materials and will discuss the correlation between device characteristics and materials properties. Photolithography-based chalcogenide-based TFTs processed by chemical bath deposition achieved mobilities in the order of 10-25 cm<sup>2</sup>/V-s. In addition, we demonstrate hybrid CMOS for a:Si-Pentacene, CdS-Pentacene and CdS-TIPS Pentacene.

We also present the impact of semiconductor thickness, gate dielectrics and contact in device performance. In addition, NAND, NOR and Inverters are demonstrated using chalcogenide-based materials integrated with either a-Si or pentacene. Device processing is carried out at a maximum processing temperature of 110oC, which is compatible with most plastic substrates.

## Tribology Focus Topic

**Room: 111 - Session TR+AS+SS-ThM**

### Atomic-scale Characterization of Tribological Interfaces

**Moderator:** S. Perry, University of Florida

8:00am **TR+AS+SS-ThM1 Electrochemical Control of Atomic Friction**, *F. Hausen*, INM - Leibniz Institute for New Materials, Germany, *A. Labuda*, McGill University, Canada, *N.N. Gosvami*, *R. Bennewitz*, INM - Leibniz Institute for New Materials, Germany

Electrochemical methods allow for fast and reversible modification of metal surfaces through deposition and dissolution of metal films, adsorption and desorption of anions, as well as oxidation and reduction. The surface composition and structure undergo dramatic changes in these processes, which should cause significant changes in the friction on the surface.

We present friction force measurements at the nanometer scale on Au(111) and Au(100) single crystal electrodes performed by means of friction force microscopy in various electrolytes. The resolution of atomic stick-slip events in an electrochemical cell is improved by the development of a dedicated instrument [1]. A significant difference in friction is found for the bare electrodes compared to the modified surfaces. Friction is extremely weak and exhibits almost no load dependence on clean Au(111) surfaces. Upon electrochemical oxidation of the surface, significant friction with linear load dependence is observed. This process is reversible and allows switching repeatedly between high and low friction [2]. In the regime of anion adsorption our results indicate a frictional response with threshold behaviour. The threshold depends on both applied normal load and the electrochemical potential [3].

After deposition of copper on gold by underpotential deposition in perchloric acid, the atomic stick-slip changes into a periodicity which indicates frictional response of CuCl with a linear load dependence. In chloride-free sulphuric acid a different behaviour is found, indicating competing effects of ion adsorption on friction forces at small scales.

[1] A. Labuda et al., Rev. Sci. Instruments 81, 083701 (2010)

[2] A. Labuda et al., Langmuir (2011), available online

[3] F. Hausen et al., Electrochimica Acta (2011), in print

8:20am **TR+AS+SS-ThM2 Surface Alterations Effects on Ice Adhesion Strength**, *C. Ellis-Terrell*, *M. Miller*, Southwest Research Institute, *M. Zou*, University of Arkansas at Fayetteville, *R. Wei*, Southwest Research Institute, *S. Beckford*, University of Arkansas at Fayetteville, *G. Hatton*, Shell Global Solutions, Inc.

Ice adhesion is a serious problem in areas such as the oil, gas, and automotive industry, telecommunications and power line transmission. There is a significant amount of research directed towards designing a coating to reduce ice accumulation. This study focuses on measuring the effects of surface roughness and surface energy on ice adhesion strength. Surface texturing ranged from high to low surface roughness. A sandblasting technique was applied to the aluminum surface creating a high surface roughness. Surface energy changes were created by depositing a silicon doped hydrocarbon film, using plasma enhanced vapor deposition. A

custom built apparatus was employed to specifically measure the adhesion force of an ice droplet. The results illustrate that the smoother as-received surfaces have lower ice adhesion strength than the rougher sandblasted surfaces.

8:40am **TR+AS+SS-ThM3 Atomistic Simulations of Nanoindentation and Nanoscratching of SiO<sub>2</sub>/Si and HfO<sub>2</sub>/Si Systems using COMB Potentials**, *T.-R. Shan*, *X. Sun*, *S.R. Phillpot*, *S.B. Sinnott*, University of Florida

Oxides such as SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and HfO<sub>2</sub>, are typically used together with Si in many high-performance electronic devices, including metal-oxide-semiconductor (MOS) devices/junctions and micro- and nano-electromechanical systems (MEMS/NEMS). The lack of precise control over mechanical properties can lead to the degradation of these materials. It is therefore critical to understand the nanometer-scale mechanical properties of materials or complex systems being considered for use in electronic devices. Nanoindentation and nanoscratching are important methods for investigating the mechanical behavior of small volumes of materials, such as thin film systems. Here, classical molecular dynamics simulations are used to examine the responses to nanoindentation and nanoscratching of thin films of SiO<sub>2</sub> and HfO<sub>2</sub> on silicon substrates. The goal is to determine the influence of thin film types and the structure of thin film and substrate interface on the responses. Because these systems consist of heterogeneous interface with significant changes in bonding as one crosses from one side of the interface to the other, the empirical charge optimized many-body (COMB) potential as implemented in large-scale atomic/molecular massively parallel simulator (LAMMPS) program is used to model the structural evolution, mechanical response and charge transfer in these systems in response to a nanometer-scale spherical indenter. Aspects of the SiO<sub>2</sub>/Si and HfO<sub>2</sub>/Si interfaces during nanoindentation and nanoscratching, including the mechanisms by which fracture and plasticity occurs, will also be addressed. We gratefully acknowledge the support of the National Science Foundation through grant numbers DMR-0426870 and DMR-1005779).

9:00am **TR+AS+SS-ThM4 Accelerated Molecular Dynamics Simulations of Nanoscale Friction**, *W.K. Kim*, University of Minnesota, *M.L. Falk*, Johns Hopkins University **INVITED**

Accelerated molecular dynamics simulations are implemented to model the sliding process of atomic force microscope experiments and to lower the sliding speeds below those in a conventional MD simulation. In this study the hyperdynamics method, originally devised to extend MD time scales for non-driven systems, is applied to the frictional sliding system. This technique is combined with a parallel algorithm that simultaneously simulates the system over a range of slider positions so that the overall acceleration rate is approximately the number of processors multiplied by the boost factor from the hyperdynamics method. The new methodologies are tested using two-dimensional and three-dimensional Lennard-Jones AFM models. The methodology is then applied to simulated sliding between an oxidized silicon tip and surface achieving a range of six decades of velocity and reproducing the experimentally observed velocity dependence of the friction force. In doing so we learn something new about this system and about friction between amorphous surfaces in general. Unlike in the crystalline case, as increasing force is applied to the amorphous tip intermediate states arise. These intermediate states serve as critical transition pathways. The emergence of such states leads to the emergence of a plateau in sliding velocity at lower sliding speeds and higher temperatures. A simple theory based on these observations successfully describes both the experimental and the simulated data.

9:40am **TR+AS+SS-ThM6 Molecular Dynamics Simulations of Contact between Carbon-Based Materials: Isolating the Effects of Experimental Variables**, *J.A. Harrison*, *K.E. Ryan*, *P.L. Keating*, US Naval Academy, *D.S. Grierson*, *J. Liu*, *K.T. Turner*, University of Wisconsin Madison, *R.W. Carpick*, University of Pennsylvania

The behavior of nanoscale contacts is complex and often cannot be understood through continuum mechanics alone. Here, parallel molecular dynamics (MD) simulations using the AIREBO potential for hydrocarbons to model indentation and friction, are used to investigate nanoscale contacts of carbon-based materials, such as diamond, DLC, and ultrananocrystalline diamond (UNCD). Specifically, the contact of carbon-based AFM probes is simulated to understand the effects of experimental parameters, including tip geometry and material selection, on the adhesion between the tip and sample. Results from the MD simulations will be compared to and discussed within the context of the complementary atomic force microscope experiments and finite element simulations. The tribological response of carbon-based materials is very sensitive to environmental conditions. For example, the presence of water has been shown to negatively impact the friction performance of hydrogenated DLCs but to improve the performance of nanocrystalline and ultrananocrystalline diamond. We have been working



to develop a potential energy function that is capable of modeling carbon-based materials in the presence of water. This talk will also outline our current efforts at potential development.

10:40am **TR+AS+SS-ThM9 Modeling the Pressure Dependence of Shear Strength in Sliding, Boundary-Layer Friction.** *M. Garvey, M. Weinert, W.T. Tysoe*, University of Wisconsin-Milwaukee

The pressure dependence of the shear strength of model alkali halide lubricant systems has been investigated at the density functional theory level. This is compared to the experimental dependence given by  $S = S_0 + \alpha P$ , where  $P$  is the contact pressure,  $S_0$  is the zero-pressure shear-strength and  $\alpha$  is the coefficient of pressure dependence. Sliding potentials were calculated and shear is found to occur between the film and the sliding interface. The heights of the potentials were calculated as a function of compression, allowing the lateral force to be calculated as a function of pressure. The calculated values of  $S_0$  and  $\alpha$  are in good agreement with experimental data.

11:00am **TR+AS+SS-ThM10 Lubrication Mechanisms of MoS<sub>2</sub> Fullerene-Like Nanoparticles: Coupling Computer and Experimental Works.** *E.W. Bucholz*, University of Florida, *I. Lahouij, F. Dassenoy*, Ecole Centrale de Lyon, France, *S.B. Sinnott*, University of Florida, *J.M. Martin*, Ecole Centrale de Lyon, France

Inorganic fullerene (IF)-like MoS<sub>2</sub> nanoparticles have been shown to be good lubricating and anti-wear additives when dispersed in a base oil. This improved tribological performance appears to be a result of the size and structure of the nanoparticles along with the test conditions. Possible lubrication mechanisms include pure rolling to sliding to the exfoliation of lamellar MoS<sub>2</sub> sheets inside the contact. *In situ* transmission electron microscopy (TEM) experiments have been used to manipulate individual MoS<sub>2</sub> nanoparticles and investigate their responses to compression and friction under different conditions. However, the very small scale of the MoS<sub>2</sub> nanoparticles makes distinguishing the properties which affect the lubrication mechanism exceedingly difficult; thus, a computational approach is used to more fully understand the most important mechanisms. Therefore, classical molecular dynamics (MD) simulations of individual nested MoS<sub>2</sub> nanoparticles are performed where they are subjected to compression and shear forces between sulfur-terminated molybdenum surfaces. Two specific nanoparticle configurations are considered, with both structures containing three layers. The first configuration is a curved, ellipsoidal MoS<sub>2</sub> nanoparticle structure with a major and minor diameter of approximately 8.9 and 6.6nm, respectively. The second nanoparticle configuration is an octahedron with grain boundaries that are approximately 6.2 nm in length. MD simulations of these structures indicate the role of curved and faceted morphologies as well as grain boundaries on the rolling/sliding behavior and nanosheet exfoliation of the particles. The results are used to interpret the experimental TEM findings and predict the dominant mechanisms associated with enhanced lubrication through the addition of these particles to base oils. This work is supported by the Office of Naval Research .

11:20am **TR+AS+SS-ThM11 Shape-Independent Lateral Force Calibration.** *E.V. Anderson, N.A. Burnham*, Worcester Polytechnic Institute

The primary problem with lateral force microscopy (LFM) has been the difficulty in calibrating the cantilever and tip in order to obtain quantitative friction data. Two recent review articles and several research articles have expressed this difficulty and the need for a simple, universally-accepted method [1,2]. The available procedures have numerous limitations. Some require specialized samples or setups. Others are difficult to perform. A number are indirect, or only suitable for certain cantilevers. Several risk damage to the tip or sample, or both, and might require the geometry of the cantilever, which can be hard to measure. We present a procedure that alleviates these problems [3]. The linear relationship between the detected voltage and lateral force is exploited to obtain the slope (calibration factor) and intercept that convert voltage to lateral force. The method is independent of sample shape, probe shape, and scan parameters (load force, gain, and scan rate). The accuracy was investigated on an order-of-magnitude level and was within 50% of torsional spring constants obtained from geometry, and the precision was under 10%. Small scan areas were also found to produce accurate calibration factors and could help to limit tip-sample wear. Quantification of nano-Newton friction forces might now become routine.

1. M. L. B. Palacio, B. Bhushan, *Crit. Rev. Solid State Mater. Sci.* **2010**, *35*, 73-104.

2. M. Munz, *J. Phys. D: Appl. Phys.* **2010**, *43*, 063001.

3. E.V. Anderson, S. Chakraborty, T. Esformes, D. Eggiman, C. DeGraf, K. M. Stevens, D. Liu, and N.A. Burnham, "Shape-Independent Lateral Force Calibration," submitted April 2011.

11:40am **TR+AS+SS-ThM12 Atomic Stick-Slip Friction Studied by Optimally-Matched Accelerated MD Simulations and AFM Experiments.** *Y. Dong*, Purdue University, *Q. Li, R.W. Carpick*, University of Pennsylvania, *A. Martini*, Purdue University

Atomic-scale stick-slip friction of platinum on gold (111) surface is quantitatively studied both experimentally and through optimally-matched accelerated molecular dynamics (MD). In order to make a direct comparison between simulation and experiment, many other factors are matched as closely as possible, such as misalignment, size effect of the tip, cantilever compliance, normal load and so on. The Parallel Replica Dynamic Method (ParRep) is used to accelerate the simulation so scan velocities can be decreased to scales approaching those used in atomic force microscope experiments. A logarithm dependence of friction on scanning velocity is observed both in Atomic Force Microscope (AFM) and MD reveals that at low speed the atomic friction lies in thermal activation regime. A further comparison shows that AFM and MD provide consistent energetics, which supports that MD can be used to interpret AFM results; but attempt frequencies differ by orders of magnitude, which is attributed to the inertia discrepancy.

# Thursday Afternoon, November 3, 2011

## Spectroscopic Ellipsometry Focus Topic

Room: 209 - Session EL+AS+EM+MS+PS+TF-ThA

### Spectroscopic Ellipsometry for Photovoltaics, Metals and Oxide Thin Films

**Moderator:** M. Creatore, Eindhoven University of Technology, the Netherlands

#### 2:00pm EL+AS+EM+MS+PS+TF-ThA1 Applications of Ellipsometry in Photovoltaics, D. Levi, National Renewable Energy Laboratory INVITED

With the growing possibility of anthropomorphic-induced climate change there has come increasing concern over energy-related emissions of carbon dioxide into the atmosphere. The search for low or no-carbon energy sources has intensified. This has led to a twenty first century gold rush into photovoltaics research and technology startups. Although the PV industry has maintained its exponential growth rate through the global economic downturn, electricity from photovoltaics is still a long ways from economic competitiveness with fossil fuel-based electricity sources. The U.S. Department of Energy recently announced the Sunshot program, with the expressed goal of \$1/Watt installed cost for utility scale PV plants by 2017. This aggressive goal will require radical advances in new and existing PV technologies.

This presentation will begin with an overview of the major PV technologies and the state of the rapidly evolving global photovoltaics industry. Photovoltaics is a natural arena for application of spectroscopic ellipsometry. Nearly all PV devices are made of multiple thin films of semiconductors and transparent conducting oxides. New materials are constantly being introduced. Film thickness, optical properties, interfaces, electronic properties, and film growth dynamics are all critical aspects of these devices and lend themselves to investigation through the use of spectroscopic ellipsometry. I will present several case studies of how we have applied spectroscopic ellipsometry in our research in photovoltaics at the National Renewable Energy Laboratory.

#### 2:40pm EL+AS+EM+MS+PS+TF-ThA3 Comparison between Ex Situ and Real Time Spectroscopic Ellipsometry Measurements of Structurally Graded Si:H Thin Films, N.J. Podraza, University of Toledo

Analysis of spectroscopic ellipsometry measurements of graded thin films remains challenging, although analysis procedures and software have improved over the past several decades. Practical use of these processes remains somewhat time consuming and is often not fully utilized by the casual user. In this work, ex situ ellipsometric spectra collected for static samples and real time spectroscopic ellipsometry (RTSE) measurements collected during film growth will be compared to illustrate differences in results arising from the measurement procedures and analysis. As an application, consider hydrogenated silicon (Si:H) thin films used for solar cells. Devices typically incorporate either amorphous silicon (a-Si:H) or "nanocrystalline" silicon (nc-Si:H) absorber layers, although the best "nanocrystalline" absorber layers actually consist of mixed-phase amorphous+nanocrystalline (a+nc) material. Si:H thin films may initially (i) nucleate as amorphous and remain amorphous throughout growth; (ii) immediately nucleate as nanocrystallites; or (iii) initially evolve in the amorphous regime but nucleate crystallites which subsequently grow preferentially over the surrounding amorphous material until nanocrystallite coalescence. Analysis of ellipsometric spectra collected for (i) or (ii) simply involve using a substrate / bulk film / surface roughness model and complex dielectric function spectra ( $\epsilon = \epsilon_1 + i\epsilon_2$ ) for the bulk material. For (iii), RTSE is ideally used to monitor the growth of Si:H that evolves through the amorphous, nanocrystalline, and mixed-phase regimes and a virtual interface analysis (VIA) procedure is used to extract  $\epsilon$  for the amorphous and nanocrystalline components, the bulk and surface roughness thicknesses versus time, and the nanocrystalline fraction depth profile in the (a+nc) growth regime. For (a+nc)-Si:H films only measured with a single static ex situ measurement at the end of the deposition, obtaining  $\epsilon$  and structural parameters of the film become less precise. Specifically, sensitivity to the variation in the nanocrystallite fraction with thickness may be lost and inaccurate  $\epsilon$  for the component materials may be obtained. This work seeks to compare the structural and optical properties of (a+nc)-Si:H obtained by RTSE and VIA with those from analysis of static ex situ spectra with models using different structures, parameterizations in  $\epsilon$ , and spectral range restrictions. These comparisons will be used to identify appropriate structural and dielectric function models to more accurately analyze

structurally graded thin films under different material and measurement circumstances.

#### 3:00pm EL+AS+EM+MS+PS+TF-ThA4 Real-Time Spectroscopic Ellipsometry of Cu(In,Ga)Se<sub>2</sub> Thin Film Deposition: Copper Transition in 3-Stage Co-Evaporation Process, D. Attygalle, University of Toledo, V. Ranjan, Old Dominion University, P. Aryal, University of Toledo, S. Marsillac, Old Dominion University, R.W. Collins, University of Toledo

With record efficiencies above 20%, Cu(In,Ga)Se<sub>2</sub> (CIGS) based solar cells have shown the greatest potential for success among the thin film photovoltaics technologies. Thermal co-evaporation of individual elements has proven to produce extremely high quality CIGS materials, provides a high level of flexibility, but also generates greater challenges in process optimization. The limitations of existing process monitoring capabilities, hence the challenge of correcting process fluctuations in real time, has led the industrial community toward more controllable CIGS deposition processes. Real time spectroscopic ellipsometry (RTSE) can be used successfully in the monitoring of complicated processes -- including CIGS film preparation by co-evaporation using precursor films of (In<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub>. Information extracted from RTSE includes the evolution of bulk layer and surface roughness layer thicknesses, the composition and phase, as well as the layer dielectric functions, all of which can assist in understanding the fabrication process and in optimizing solar cells. In this study, the focus is on the transitions of Cu-poor to Cu-rich CIGS and vice versa by observing the changes in ( $\psi$ ,  $\Delta$ ) spectra obtained by RTSE. The commonly used monitoring method, which involves observing the changes in emissivity of the film, largely depends on the apparatus design, the substrate, and the bulk layer thickness. When a CIGS film is prepared by exposing a precursor film of (In<sub>x</sub>Ga<sub>1-x</sub>)<sub>2</sub>Se<sub>3</sub> to Cu and Se fluxes, thereby becoming Cu-rich, a semi-liquid Cu<sub>2-x</sub>Se phase is believed to form on top of a bulk layer consisting of mixed phases of Cu(In,Ga)Se<sub>2</sub> and Cu<sub>2-x</sub>Se [1]. A multilayer optical model, with appropriate effective medium approximation layers to represent this scenario, has shown good agreement with the observed ( $\psi$ ,  $\Delta$ ) spectra. Since RTSE is highly sensitive to monolayer-level changes in the top-most layer, RTSE gives superior sensitivity in Cu-rich to Cu-poor end point detection, which occurs when the top Cu<sub>2-x</sub>Se phase drops below detectable limits. Furthermore this method is less affected by the substrate and bulk layer thickness. Although careful analysis of RTSE can give a wealth of information about CIGS material properties and their evolution, this type of end point detection can be successful simply by monitoring the real time changes in the ( $\psi$ ,  $\Delta$ ) spectra.

[1] J. AbuShama, R. Noufi, Y. Yan, K. Jones, B. Keyes, P. Dippo, M. Romero, M. Al-Jassim, J. Alleman, and D.L. Williamson, "Cu(In,Ga)Se<sub>2</sub> Thin-film evolution during growth from (In,Ga)<sub>2</sub>Se<sub>3</sub> precursors", *Mat. Res. Soc. Symp. Proc.* paper H7.2.1, (2001).

#### 3:40pm EL+AS+EM+MS+PS+TF-ThA6 Bulk Heterojunction Solar Cell Characterization by Phase Modulated Spectroscopic Ellipsometry, K. Uppreddi, L. Yan, HORIBA Scientific

The blend morphology, phase separation as well as crystallinity of organic photovoltaic solar cell are important properties to increase the efficiency. The performance of such cells is strongly influenced by blend composition and thermal annealing conditions. In this work we demonstrate the use of ellipsometry as a powerful and sensitive metrology means of monitoring organic solar cell based on the blend of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM). Ellipsometric measurements were performed on P3HT/c-Si, PCBM/c-Si and P3HT:PCBM/c-Si at an angle of incidence of 70 degree, across the spectral range 190 – 2100 nm (0.6-6.5 eV). Two different analysis protocols were used to model the P3HT:PCBM blend structure. In the first protocol effective medium theory was used to represent the optical constant of layer, where as in the second one the blend was treated as one single homogenous material. The approach renders investigation of final morphology and composition.

#### 4:00pm EL+AS+EM+MS+PS+TF-ThA7 In Situ Spectroscopic Ellipsometry during Atomic Layer Deposition of Pt, Pd and Ru, N. Leick, J.W. Weber, M.J. Weber, A.J.M. Mackus, H.C.M. Knoops, W.M.M. Kessels, Eindhoven University of Technology, Netherlands

The precise thickness control of atomic layer deposition (ALD) and its conformal growth make ALD the method of choice for nanometer thin film deposition. Platinum-group metals such as Pt, Pd and Ru have many applications in the areas of nanoelectronics and catalysis and recently there has been considerable interest to deposit films of these materials by ALD. Spectroscopic ellipsometry (SE) is a powerful, noninvasive optical technique that can be used *in situ* during ALD to precisely monitor the thickness of the films. SE also provides information on the optical and

electrical properties of the films which is very relevant for their applications. Choi et al. [1] previously investigated the dielectric functions of Pt-group metal films with a thickness of ~400 nm as prepared by physical vapor deposition. For the aforementioned applications, however, the films are required to be much thinner, which leads to differences in film morphology as well as to dielectric functions that can be different from those of bulk films. In the spectroscopic ellipsometry work to be presented in this contribution we have therefore focused on films with thicknesses from 5 nm to 35 nm. *In situ* data was obtained during ALD in the photon energy range of 0.7 – 6.5 eV. Using a Kramers-Kronig consistent B-spline model to account for the thickness-dependent dielectric functions, we were able to obtain accurate ALD growth-per-cycle values for Ru, Pt and Pd ( $1.00 \pm 0.06 \text{ \AA}$ ,  $0.47 \pm 0.04 \text{ \AA}$ ,  $0.14 \pm 0.02 \text{ \AA}$ ). Furthermore, the contributions from free-carriers (Drude term) and interband absorptions (Lorentz-oscillator contributions) were investigated by combining the SE data with FT-IR reflectance data such that the photon energy range of 0.04 eV – 6.5 eV was covered. In this range, it was possible to represent each film with a unique Drude-Lorentz model although some ambiguities about the Lorentz oscillator contributions remained in the case of Ru. It will be shown that the extracted thicknesses and electrical resistivities from this model are in line with data obtained from X-ray reflectometry and four-point probe measurements (for example Ru:  $\rho_{SE} \sim 23 \mu\Omega\cdot\text{cm}$  and  $\rho_{FPP} \sim 16 \mu\Omega\cdot\text{cm}$ ). Furthermore, in the case of Ru also the influence of the film roughness will be addressed.

[1] Choi et al., Phys. Rev. B **74**, 205117 (2006)

4:20pm **EL+AS+EM+MS+PS+TF-ThA8 Manipulating the Optical Properties of Metals: Sculptured Thin Films Coated by Atomic Layer Deposition**, D. Schmidt, N. Ianno, E. Schubert, M. Schubert, University of Nebraska - Lincoln

The fabrication of three-dimensional metal nanostructures with tailored geometry is one of the central challenges of nanotechnology because geometrical and material parameters are responsible for the optical, electrical, mechanical, chemical, or magnetic properties of such nanostructured thin films. Engineered artificial sculptured thin films (STFs) with designed anisotropies are potential candidates for applications in various fields such as optics, magneto-optics, as well as chemical and biological sensing and detection. However, in order to utilize metallic nanostructures for novel applications their size-, structure-, and material-driven physical properties have to be understood and quantified.

We utilize glancing angle electron-beam deposition, which exploits physical atomic-scale shadowing and dynamically varying particle flux azimuth for fabrication of three-dimensional highly spatially coherent STFs with different morphologies. Subsequently, nanostructures are individually covered with a thin conformal coating (cladding) by means of atomic layer deposition (ALD).

We will present the anisotropic optical properties of highly anisotropic ALD coated metal STFs determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region. The analysis of our multilayer slanted columnar thin films deposited at glancing angle ( $\theta_i = 85^\circ$ ) revealed that such STFs possess monoclinic optical properties, and the optical response may be described by an effective medium dielectric homogenization approach. It will be discussed how the anisotropic Bruggeman effective medium approximation (AB-EMA) allows for determination of structural parameters as well as fractions of individual film constituents. Furthermore, the AB-EMA analysis reveals that the anisotropic dielectric properties of the metal core changes upon deposition of a dielectric cladding.

4:40pm **EL+AS+EM+MS+PS+TF-ThA9 Ellipsometric Characterisation of Porous Aluminium Oxide Supports**, W. Ogieglo, N.E. Benes, H. Wormeester, MESA+ Institute for Nanotechnology, University of Twente, Enschede, The Netherlands

Porous aluminium oxide is widely used as a support material for thin film inorganic micro- and mesoporous membranes. Such membranes are used in energy-efficient gas separation, pervaporation and nanofiltration processes. Ellipsometry can be used to determine material properties of the thin membrane films, as well as the penetrant loading [1]. Interpretation of the ellipsometry data requires a detailed knowledge of the porous aluminium oxide support. This support is made of aluminium oxide particles that are sintered together. In between the particles voids are present that amount to 38% porosity. We have studied the influence of the size of the voids on the optical response of the support material. For this study, voids with a diameter of around 60, 80 and 160 nm were used. We noted a strong decrease of the normal incidence specular reflection with void size and a subsequent increase in off specular reflection. In ellipsometry, only a limited depolarization of the specular reflected light was noted in the wavelength range between 300 and 1750 nm. The angle dependent ellipsometry measurements showed that the optical properties of these

supports can not be obtained from a direct inversion. The reason for this is that at the interface the more or less spherical voids are cut, which leads to a distribution of openings at the surface, i.e., a substrate with a very rough surface. This roughness was modelled with a graded porosity changing from 38% in the bulk to 75% at the outer surface. This measured variation in porosity is very similar to the cumulative height distribution of the surface layer obtained from AFM. The validity of this graded porosity model was verified from the analysis of a sample with a thin polysulfone (PSU) layer deposited on the support. The PSU layer partly fills the open pores at the surface. This results in an interface with a graded variation in aluminium oxide, void and PSU.

The proper treatment of the surface layer also provides the optical properties of the porous aluminium oxide bulk material itself. These optical properties can in a limited wavelength range be modelled with Bruggeman's effective medium approximation. As a consequence of the size of the inclusions, their diameter is no longer negligible with respect to the wavelength of light in the UV part of the spectrum. For the material with the largest pore size, also a large part of the visible range has to be excluded. A more elaborate approach than the standard effective medium approach has to be used in this case.

[1] H. Wormeester, N.E. Benes, G.I. Spijksma, H. Verweij and B. Poelsema Thin Solid Films **455-456**, 747-751 (2004)

5:00pm **EL+AS+EM+MS+PS+TF-ThA10 Optical Properties and Structure of Vanadium Oxide Thin Films**, M.A. Motyka, M.W. Horn, Pennsylvania State University, N.J. Podraza, University of Toledo

Vanadium oxide ( $\text{VO}_x$ ) thin films are common materials used as imaging layers in uncooled microbolometer based thermal imaging devices. These films are used in this application largely due to the controllable resistivity of the film ( $\rho$ ), the high temperature coefficient of resistance (TCR), and the low electrical noise. One of the main difficulties of this material system relates to the multiple valence states of vanadium, each of which results in materials with different electrical properties. Bolometer quality  $\text{VO}_x$  may consist of a composite of nanocrystalline face centered cubic (FCC) VO phase and amorphous materials. The thin film oxygen content via Rutherford back scattering (RBS) has suggested that the typical ratio V:O should be near 1:1.7-2.0, significantly higher than the stability window of the FCC phase. This off-stoichiometry ratio suggests that the amorphous material is a mixture of higher oxygen valence states similar to  $\text{V}_2\text{O}_5$  and  $\text{VO}_2$ . The higher quality  $\text{VO}_x$  thin film material also has been observed via transmission electron microscopy (TEM) to contain  $\text{VO}/\text{V}_2\text{O}_5$  nano-twin crystalline domains. The presence of each of these phases impacts the electrical and optical properties of the resulting  $\text{VO}_x$  film. Films with various oxygen contents and structures were studied with spectroscopic ellipsometry (SE) over a spectral range of 0.05 to 5.15 eV using a multichannel dual rotating compensator near-ultraviolet to near infrared instrument in conjunction with Fourier transform infrared spectroscopic ellipsometry (FTIR-SE). Thus, the complex dielectric function spectra ( $\epsilon = \epsilon_1 + i\epsilon_2$ ) can be obtained for these materials over the full spectral range. Differences in  $\epsilon$  due to variations in the film structure are observed as functions of processing, indicating that SE is a means of probing the material composition and structure. Specifically,  $\epsilon$  are compared for various film composites fabricated by unbiased pulsed DC magnetron sputtering as well as composite films prepared by reactive ion beam sputtering and pulsed DC magnetron sputtering with a substrate bias. The microstructure and  $\epsilon$  are correlated with films exhibiting the desirable device electrical properties. In situ real time spectroscopic ellipsometry (RTSE) has shown that environmental conditions alter the as-deposited  $\text{VO}_x$  thin films grown via pulsed DC-magnetron reactive sputtering of a metallic vanadium target. In order to prevent undesired atmospheric effects to the thin film, it is a common practice to encapsulate the thin film with a more environmentally stable material. In this study, the material chosen was  $\text{SiO}_2$  grown in the same deposition chamber, pre-atmospheric exposure, via rf sputtering.

5:20pm **EL+AS+EM+MS+PS+TF-ThA11 Sensitivity of Dielectric Properties of Vanadium Dioxide Thin Films to Growth Conditions**, D.W. Ferrara, R.E. Marvel, J. Nag, R.F. Haglund, Vanderbilt University

Vanadium dioxide ( $\text{VO}_2$ ) is a strongly-correlated electron material with a well-known semiconductor-to-metal transition (SMT) that can be induced thermally ( $T_c = 68^\circ\text{C}$ ), optically, or electrically. Recently,  $\text{VO}_2$  films have attracted attention as a component in active metamaterials, especially in conjunction with metal nanostructures. Since these structures are highly sensitive to the dielectric properties of the embedding material, the SMT of  $\text{VO}_2$  can be used to tune the optical response of the structure. Accurately modeling the behavior of these structures requires detailed knowledge of the dielectric function of  $\text{VO}_2$  as it undergoes the SMT; however, previous measurements of the optical constants of  $\text{VO}_2$  reveal significant variations between experiments.

To understand systematic variations due to growth conditions, films of VO<sub>2</sub> were deposited on either silicon, glass, or sapphire substrates by pulsed laser ablation of vanadium metal targets in 10 mTorr oxygen (O<sub>2</sub>) background gas, followed by annealing at 450°C in 250 mTorr of O<sub>2</sub>. Anneal times were varied from 30 to 90 depending on film thickness; deposition thickness was varied from 20 nm to 200 nm. For each sample, temperature-dependent spectroscopic ellipsometry measurements at optical and near-infrared wavelengths were conducted to determine the dependence of the optical constants on film thickness, substrate and crystallinity, and temperature.

Bruggeman and Maxwell-Garnett effective-medium formulations were used to account for three constituent materials: semiconducting VO<sub>2</sub>, metallic VO<sub>2</sub>, and vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>). The effective dielectric functions were modeled using Lorentz and Tauc-Lorentz oscillators. Our results show that the contribution of V<sub>2</sub>O<sub>5</sub> to the effective dielectric function increases with annealing time, consistent with previous studies. The results are also substantiated using Rutherford backscattering, X-ray photoelectron spectroscopy and X-ray diffraction.

# Friday Morning, November 4, 2011

## Spectroscopic Ellipsometry Focus Topic

Room: 209 - Session EL+AS+EM+MS+PS+TF-FrM

## Spectroscopic Ellipsometry: Future Directions and New Techniques

Moderator: H. Wormeester, MESA, The Netherlands

8:20am **EL+AS+EM+MS+PS+TF-FrM1 Current Trends and Future Outlook for Spectroscopic Ellipsometry**, *J.N. Hilfiker, B. Johs, C.M. Herzinger, T.E. Tiwald, J.A. Woollam Co., Inc.* **INVITED**

This talk reviews the significant developments in spectroscopic ellipsometry (SE) in areas including extending spectral range, improving accuracy, and enhancing speed. Current SE applications owe much to hardware and software developments of the past. Thus, today's research efforts may reach full potential for applications years or even decades from now. With this in mind, we point to the current state-of-the-art and what this may mean for future SE applications.

Three important areas will be explored. First, there has been a continual trend to expand SE wavelength range. This has included extensions to both shorter and longer wavelengths. For the latter, there is current development into the THz. More immediate benefit may come from smaller SE extensions from the ultraviolet to the near infrared. For example, further near-infrared extensions help to characterize modern transparent conductive oxides (TCOs), used in both inorganic and organic photovoltaic stacks.

Second, we look at the search for improved SE accuracy. Substantial improvements have come with the development of new ellipsometer technologies, progressing from rotating analyzer/polarizer to rotating compensator and now dual-rotating compensator ellipsometers. In addition to improved accuracy, this technology provides advanced measurements, including the complete Mueller-matrix. This will open SE characterization to new applications of anisotropic, nanostructured, and even patterned thin films. Accuracy enhancements must be compatible with the expanding SE spectral range. Infrared SE has overcome many non-ideal optical components to provide measurements competitive to standard FTIR measurements.

Third, we look at the quest for improved measurement speed. This development is constrained by the previous requirements. The benefits of a wide spectral range generally outweigh speed requirements; otherwise laser-based ellipsometry would still have a strong foothold. Thus, compromises are made depending on application. Current instrumentation typically utilizes detector arrays for multi-channel SE measurements.

To conclude, we will look at the SE outlook and how it may take advantage of wavelength range, accuracy, and speed. In-line and in-situ SE measurements show special promise. Significant improvements in instrumentation, computing speed, and software are now making these applications more feasible. In addition, there are novel ideas to provide sample access and overcome non-ideal measurement conditions for in-line and in-situ SE. Significant progress in many different areas promises to extend ellipsometry into new areas – many of which are being studied by researchers today.

9:00am **EL+AS+EM+MS+PS+TF-FrM3 THz Optical Hall-effect and MIR-VUV Ellipsometry Characterization of 2DEG Properties in a HfO<sub>2</sub> Passivated AlGaIn/GaN HEMT Structure**, *S. Schöche, U. of Nebraska - Lincoln, J. Shi, Cornell U., A. Boosalis, P. Kühne, U. of Nebraska - Lincoln, C.M. Herzinger, J.A. Woollam, J.A. Woollam Co., Inc., W.J. Schaff, L.F. Eastman, Cornell U., V. Darakchieva, Linkoping U., Sweden, M. Schubert, T. Hofmann, U. of Nebraska - Lincoln*

Nitride based high electron mobility transistors (HEMT) utilize the formation of a two-dimensional electron gas (2DEG) at the interface between GaN and AlGaIn due to a difference in spontaneous polarization. It is known that surface traps significantly influence the electrical properties of this 2DEG. Accurate knowledge about the influence of surface passivation on the channel properties is crucial. The device performance is governed by the mobility, the sheet charge density, and the effective mass of electrons in the 2DEG. These parameters are typically determined by electrical Hall effect (EHE), Shubnikov-de Haas (SdH), or cyclotron resonance (CR) measurements. Commonly these experiments require very low temperatures and high magnetic fields. Complex contact configurations are required for SdH and EHE and the ability to locate the 2DEG and possible parallel current paths is limited.

We present non-contact, optical measurements of free-charge carrier mobility, sheet density, and effective mass parameters of the 2DEG for a HfO<sub>2</sub>-passivated AlGaIn/GaN HEMT structure at room temperature.

Spectroscopic ellipsometry in the spectral range from THz and Mid-IR to VUV and THz optical Hall-effect (generalized ellipsometry in magnetic field) (OHE) are employed.

The MIR measurements are performed for analysis of the heterostructure constituents' layer thickness, phonon modes, and volume free charge carriers. The phonon mode parameters were found to be in excellent agreement with literature values and the existence of significant volume charge carrier concentrations could be excluded. NIR to VUV ellipsometry is used to determine the thickness of the thin top layers. From a line-shape analysis in the VUV spectral range the optical constants of the HfO<sub>2</sub> passivation layer could be extracted. An amorphous structure of the HfO<sub>2</sub> passivation layer could be confirmed by comparison with existing studies in literature.

OHE in the THz spectral range is performed for characterization of the 2DEG channel parameters. A classical Drude model for free charge carrier contribution to the dielectric function was applied to determine the sheet density, the carrier mobility, and the effective mass of the 2DEG electrons. The electron effective mass of  $(0.22 \pm 0.04) m_0$  extracted here using OHE corroborates the values found in previous SdH and CR studies. The values for the high-frequency sheet density and carrier mobility obtained by the optical investigations in the THz spectral range are in excellent agreement with results from dc EHE measurements indicative within linear Boltzmann transport theory for frequency-independent carrier scattering mechanisms of the 2D carrier distribution.

9:20am **EL+AS+EM+MS+PS+TF-FrM4 Vector-Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films**, *D. Schmidt, C. Briley, E. Schubert, M. Schubert, University of Nebraska - Lincoln*

Sculptured thin films are self-organized and self-assembled three-dimensional nanostructures with tunable geometries. These artificial nanostructured thin films exhibit highly anisotropic physical properties, which mainly depend on their specific geometry.

Slanted, highly-spatially coherent, columnar nanostructure samples were prepared by glancing angle electron-beam deposition. Glancing angle deposition is a bottom-up fabrication technique that employs a physical vapor deposition process at oblique angles where the trajectory of the incoming particle flux is not parallel to the substrate normal. The technique allows to engineer the columnar film structure and is today amongst the most promising self-organized fabrication processes in micro- and nanotechnology.

We present and discuss the novel approach of vector-magneto-optical generalized ellipsometry on ferromagnetic permalloy nanostructured thin films carried out at room temperature. Investigations have shown that the metal alloy thin films are highly transparent, reveal strong form-induced birefringence, and exhibit intriguing magneto-optical anisotropy. Spatial magnetization orientation hysteresis and magnetization magnitude hysteresis properties are studied using a three-dimensional Helmholtz coil arrangement. This particular octupole setup allows for arbitrary magnetic field directions at the sample position with field strengths up to 200 mT while optical access is granted for reflection and transmission-type ellipsometry measurements. Analysis of data obtained within this unique vector-magneto-optic setup reveals magnetization anisotropy of the permalloy slanted nanocolumns and gives insight into switching behavior of confined magnetic domains.

9:40am **EL+AS+EM+MS+PS+TF-FrM5 THz Dielectric Anisotropy of Metal Slanted Columnar Thin Films**, *T. Hofmann, D. Schmidt, A. Boosalis, P. Kühne, R. Skomski, University of Nebraska-Lincoln, C.M. Herzinger, J.A. Woollam, J.A. Woollam Co., Inc., M. Schubert, E. Schubert, University of Nebraska-Lincoln*

Sculptured thin films (STFs) present an interesting class of self-organized, artificially made materials with three-dimensional, highly spatially coherent arrangements of nanostructures. Contemporary interest in materials for terahertz (THz) electronic, optoelectronic, and optical applications is redrawing attention to STFs that may enable designed optical properties for the THz frequency region.

We report on the anisotropic optical dielectric functions of a metal (cobalt) slanted columnar thin film deposited by electron-beam glancing angle deposition for the THz frequency domain using generalized spectroscopic ellipsometry. A simple anisotropic Bruggeman effective medium dielectric function homogenization approach is successfully employed to describe the observed optical response. This approach describes isolated, electrically conductive columns which render the thin film biaxial (orthorhombic). The anisotropy induced by the columnar film structure is very large. The anisotropic Bruggeman effective medium approach predicts upon slight modifications of Drude, fraction and/or depolarization parameters that

targeted optical properties of STF in the THz range can be achieved by variation of slanting angle, lateral column density, and material.

10:00am **EL+AS+EM+MS+PS+TF-FrM6 A Compact High-speed Spectroscopic Ellipsometer**, G. Chin, ULVAC Inc., Japan

Recently, we developed a compact, high-speed spectroscopic ellipsometer. It analyzes the spectrums obtained from the polarization interference occurring between two multiple-order retarders which snapshot the wavelength distribution of the sample's spectroscopic polarization parameters. This innovative spectroscopic ellipsometer can measure the thickness and optical constants of thin films at a dramatically fast speed. Its acquisition time is as short as 10 ms. It does not require the conventional complex mechanical or active components for polarization-control, such as a rotating compensator and an electro-optical modulator. It can open great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. For example, it was integrated into the deposition tool and successfully measured thin films in the vacuum chamber.

This paper describes the principle, system configuration and our innovative efforts on developing the compact high-speed spectroscopic ellipsometer. Some typical application data will be also introduced, such as in line and in situ measurements for photovoltaic, flat panel display and semiconductor industries.

10:20am **EL+AS+EM+MS+PS+TF-FrM7 Ellipsometry Porosimetry (EP): In Situ Spectroscopic Ellipsometry Measurements Coupled with Pressure Controlled Adsorption of Organic Vapors to Study Properties of Nano-Porous Thin Films**, J.P. Piel, L. Kitzinger, A. Bondaz, C. Defranoux, SEMILAB-SOPRALAB, France

Ellipsometric porosimetry (EP) is a non contact, non destructive technique that is cited as a reference technique for porous thin film analysis [1, 2]. As it is based on a spectroscopic ellipsometric measurement, the technique allows the precise determination of the refractive indices and thickness of the porous films. The advantage of these EP tools is that the combination of this well established spectroscopic ellipsometric (SE) technique with a suitably adapted adsorption chamber permits access to all the information obtained by classic adsorption experiments (e.g. BET) on thin films with an excellent sensitivity. Information such as open and closed porosity, pore size distribution etc... can be thus obtained.

In addition the EP allows access to a multitude of information that the classic equipment does not. For example, Spectroscopic Ellipsometry allows to follow the variation of the sample thickness during the adsorption experiment, leading to the determination of the Young's Modulus for the thin films. This will be presented. The technique is highly sensitive to the detection of interfaces; it is thus possible to detect a porosity gradient or to study a multilayer structure and thereafter simultaneously plot the two corresponding adsorption isotherms [3]. In the same manner, the instrument permits the use of a range of different gases adsorptive in order to tailor the probe molecule to the morphology and to the chemistry of the porous layer at ambient temperature [4]. We thus obtain information on the chemistry of the pores within the layer, before, during and after the adsorption experiment. Recent developments include the implementation of the FTIR interferometer SE extension to the EP system. It allows a precise characterization of the chemistry of the pores within the layer. We thus obtain information on the chemical bonds present in the layers before, during and after the adsorption experiment. Preliminary results will be presented.

Specifically, this fundamental technique permits the thorough characterization of porous thin film samples. We will demonstrate some of the different features of the EP technique with regards to the morphological and chemical properties of the porous thin films. Additionally, we will illustrate the technique for various thin film applications such as solgel thin films, nanofilms for catalysis, photovoltaic cells, fuel cells, optical sensors, and bio-compatible materials to name but a few.

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Brueckel, T.: NT+AS+MI-WeM1, **28**  
Bruener, P.: AS-WeA1, 30  
Bruix, A.: IS+AS+SS-MoM3, 4  
Brukan, M.J.: AS+BI+NS-WeM10, **26**  
Bryan, S.R.: AS-ThM11, 35; AS-TuM11, **11**; AS-TuP4, 20  
Bucholz, E.W.: TR+AS+SS-ThM10, **41**  
Bunker, K.L.: AS-TuP13, 21  
Bunning, T.J.: AS+BI+NS-WeM6, 25  
Burnham, N.A.: TR+AS+SS-ThM11, **41**  
Buschhaus, C.: AS-ThM1, 34  
Butler, L.: AS-TuA9, 15

## — C —

Calley, W.L.: IS+AS+SS-MoA6, **8**  
Cameron, C.: AS-MoA10, 7  
Camillone, N.: NS+AS-TuA10, **18**  
Camp, P.J.: NT+AS-WeA8, 33  
Candler, R.: AS-TuP22, 23  
Carlsson, P.-A.: IS+AS+SS-MoM6, 4  
Carpick, R.W.: TR+AS+SS-ThM12, 41;  
TR+AS+SS-ThM6, 40  
Carrillo-Castillo, A.: TC+AS+EM-ThM11, 39  
Castner, D.G.: AS-MoM8, 3; AS-TuA3, 14; AS-TuM6, 10; BP-SuA1, **1**  
Ceballos-Sanchez, O.: AS-TuP20, **23**  
Ceccone, G.: BI-ThM6, 36  
Chabal, Y.J.: IS+AS+SS-MoM10, 5  
Chambers, S.A.: IS+AS+SS-MoM5, 4  
Chen, D.: IS+AS+SS-MoA8, 9  
Chen, X.: AS+BI+NS-WeM9, **26**  
Chi, E.Y.: NT+AS-WeA8, **33**  
Chin, G.: EL+AS+EM+MS+PS+TF-FrM6, **46**  
Cho, S.: AS-TuP23, 23  
Choi, B.K.: AS-TuP6, 20  
Christophis, C.: IS+AS+SS-TuM6, 12  
Clark, E.A.: AS-TuP12, 21  
Coker, E.: AS-MoA8, 7  
Collins, R.W.: EL+AS+EM+MS+PS+TF-ThA4, 42  
Coults, S.J.: AS-MoM10, 3; AS-TuA7, 14; BI-ThM4, 35  
Cowell, W.: AS-MoM9, 3  
Cowin, J.P.: AS-ThM2, **34**  
Cubic, D.: AS-TuP5, **20**  
Cui, Y.: AS-MoA4, 6  
Culbertson, R.J.: BI-ThM12, **36**

## — D —

Dadson, A.: AS-WeA11, 31  
Dahint, R.: NT+AS-WeA10, **33**  
Dahn, J.: AS-MoM3, 2  
Darakchieva, V.: EL+AS+EM+MS+PS+TF-FrM3, 45  
Dassenoy, F.: TR+AS+SS-ThM10, 41  
Davis, R.: AS-WeA11, 31  
Davis, R.F.: AS-WeA7, 30  
Dawahre, N.: AS-TuA9, 15  
De Jonge, N.: AS-TuP6, 20; IS+AS+SS-TuM3, **12**;  
IS+AS+SS-TuM5, 12  
Defranoux, C.: EL+AS+EM+MS+PS+TF-FrM7, 46; EL+AS+EM+MS+PS+TF-ThM10, 38  
Deppert, K.: IS+AS+SS-MoM4, 4  
Desai, T.V.: IS+AS+SS-TuM12, 13  
Discher, B.M.: AS+BI+NS-WeM9, 26  
Dockstader, T.: TC+AS+EM-ThM6, 39  
Dolocan, A.: NS+AS-TuA10, 18  
Donath, M.: NS+AS-TuA12, 19

Dong, X.: AS-WeA8, **31**  
Dong, Y.: TR+AS+SS-ThM12, **41**  
Doolittle, W.A.: IS+AS+SS-MoA6, 8  
Droopad, R.: AS-TuP17, 22  
Droubay, T.: IS+AS+SS-MoM5, 4  
Dubey, M.: NT+AS+MI-WeM10, **29**; NT+AS-WeA8, 33  
Dufrene, Y.F.: BP-SuA5, **1**  
Durr, M.: AS-MoA3, **6**

## — E —

Eastman, L.F.: EL+AS+EM+MS+PS+TF-FrM3, 45  
Edwards, E.A.: AS-MoA11, 7  
Eichhorn, K.-J.: EL+AS+EM+MS+PS+TF-ThM1, **36**  
Eigler, D.: NS+AS-TuA2, **17**  
Eliad, L.: AS+BI+NS-WeM6, 25  
El-Khatib, S.: NT+AS+MI-WeM5, 28  
Ellingsworth, E.C.: NT+AS+MI-WeM4, **28**  
Ellis, D.: AS-TuP10, 21  
Ellis-Terrell, C.: TR+AS+SS-ThM2, **40**  
El-Zubir, O.: BI+AS+NS+SS-WeA9, 32  
Engelhard, M.H.: AS-MoA6, **6**; AS-ThM4, 34  
Engstrom, J.R.: IS+AS+SS-TuM12, 13  
Eralp, T.: IS+AS+SS-TuM9, 12  
Erkens, I.J.M.: IS+AS+SS-MoA9, **9**  
Escobar, C.A.: BI+AS+NS+SS-WeA11, **33**  
Escudero, C.: IS+AS+SS-TuM1, **11**  
Ezekoye, O.K.: AS-TuP15, **22**

## — F —

Falk, M.L.: TR+AS+SS-ThM4, **40**  
Faradzhev, N.S.: EL+AS+EM+MS+PS+TF-ThM9, 38  
Faubel, M.: IS+AS+SS-TuM11, 13  
Feici, R.: IS+AS+SS-MoM6, 4  
Feltz, A.: AS-MoM11, 3; NS+AS-TuA11, 18  
Feng, X.: IS+AS+SS-MoA8, 9  
Fenner, C.: HI+AS-TuA3, 16  
Fenske, J.: NT+AS+MI-WeM3, 28  
Ferrara, D.W.: EL+AS+EM+MS+PS+TF-ThA11, 43  
Ferreira, E.S.B.: AS-TuA2, 14  
Fischer, D.A.: AS-TuA3, 14  
Fisher, G.L.: AS-ThM1, **34**; AS-TuM11, 11  
Fleischauer, M.D.: TC+AS+EM-ThM5, 39  
Franz, S.: AS-TuP22, 23  
Frenkel, A.I.: IS+AS+SS-MoM1, **3**  
Fronheiser, J.: AS-WeA9, 31  
Fujita, D.: HI+AS+BI+NS-WeM12, 27  
Fujiyama, H.: IS-TuP1, 24

## — G —

Gamble, L.J.: AS-MoM8, 3  
Garramone, J.J.: AS+BI+NS-WeM11, **26**  
Garvey, M.: TR+AS+SS-ThM9, **41**  
Gaspar, D.J.: AS-ThM11, **35**  
Gazit, E.: AS+BI+NS-WeM6, 25  
Gazquez, J.: NT+AS+MI-WeM5, 28  
Gebhardt, C.R.: AS-MoA3, 6  
Gerasimov, J.Y.: EL+AS+EM+MS+PS+TF-ThM6, **37**  
Gerhardt, R.A.: TC+AS+EM-ThM10, 39  
Giannuzzi, L.: HI+AS-TuA11, **17**  
Giewekemeyer, K.: IS+AS+SS-TuM6, 12  
Gilmore, I.S.: AS-MoA9, 7; AS-TuM4, 10  
Givler, B.C.: NT+AS-WeA8, 33  
Gnade, B.E.: TC+AS+EM-ThM11, 39  
Goacher, R.E.: AS-MoA11, **7**  
Gözlhäuser, A.: HI+AS+BI+NS-WeM6, 27  
Gordon, R.J.: AS-MoA4, 6  
Gorniak, T.: IS+AS+SS-TuM6, **12**  
Gosvami, N.N.: TR+AS+SS-ThM1, 40  
Goyette, R.: NT+AS+MI-WeM5, 28  
Graham, D.J.: AS-TuM6, **10**  
Graham, G.W.: AS-TuP15, 22

Grantham, S.: EL+AS+EM+MS+PS+TF-ThM9, 38  
 Grass, M.E.: IS+AS+SS-MoM4, 4; IS+AS+SS-TuM9, 12  
 Green, F.M.: AS-MoA9, 7  
 Greenlee, J.D.: IS+AS+SS-MoA6, 8  
 Greenwood, O.: AS-TuA4, 14  
 Grehl, T.: AS-WeA1, 30  
 Grierson, D.S.: TR+AS+SS-ThM6, 40  
 Grönbeck, H.: IS+AS+SS-MoM4, 4; IS+AS+SS-MoM6, 4  
 Grunze, M.: IS+AS+SS-TuM6, 12  
 Guenther, B.: NS+AS-TuA11, 18  
 Guo, H.X.: HI+AS+BI+NS-WeM12, 27  
 Gustafson, J.: IS+AS+SS-MoM4, 4; IS+AS+SS-MoM6, 4

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Hadjar, O.: AS-MoA10, 7  
 Haglund, R.F.: EL+AS+EM+MS+PS+TF-ThA11, 43  
 Halevi, B.: AS-TuP3, 20  
 Hallberg, T.: EL+AS+EM+MS+PS+TF-ThM4, 37  
 Hamers, R.J.: BI+AS+NS+SS-WeA3, 31  
 Hammer, G.E.: AS-MoM8, 3  
 Hammond, J.S.: AS-ThM10, 35; AS-TuM1, 10; AS-TuM11, 11; AS-TuP19, 22  
 Hanley, L.: AS-MoA4, 6  
 Hanuš, J.: BI-ThM6, 36  
 Happel, M.: IS+AS+SS-MoM3, 4  
 Hara, K.: IS-TuP1, 24  
 Harl, R.R.: AS-ThM3, 34; AS-WeA10, 31; BI+AS+NS+SS-WeA10, 32  
 Harris, N.: AS-TuA9, 15  
 Harrison, J.A.: TR+AS+SS-ThM6, 40  
 Hart, M.A.: BI-ThM12, 36  
 Hatton, G.: TR+AS+SS-ThM2, 40  
 Hausen, F.: TR+AS+SS-ThM1, 40  
 Havercroft, N.: AS-TuM5, 10; AS-WeA1, 30  
 He, C.: NT+AS+MI-WeM5, 28  
 Held, G.: IS+AS+SS-TuM9, 12  
 Hellman, A.: IS+AS+SS-MoM6, 4  
 Hemminger, J.C.: IS+AS+SS-TuM11, 13  
 Henderson, W.E.: IS+AS+SS-MoA6, 8  
 Hennies, F.: IS+AS+SS-MoM9, 5  
 Henry, K.L.: AS-TuA8, 15  
 Herbots, N.X.: BI-ThM12, 36  
 Hernandez, G.: AS-TuP22, 23  
 Herrera-Gomez, A.: AS-MoM5, 2; AS-TuP20, 23; AS-TuP21, 23  
 Herzing, A.A.: AS-TuA8, 15  
 Herzinger, C.M.: EL+AS+EM+MS+PS+TF-FrM1, 45; EL+AS+EM+MS+PS+TF-FrM3, 45; EL+AS+EM+MS+PS+TF-FrM5, 45  
 Hildebrand, H.: AS-TuP19, 22  
 Hilfiker, J.N.: EL+AS+EM+MS+PS+TF-FrM1, 45  
 Hill, S.B.: EL+AS+EM+MS+PS+TF-ThM9, 38  
 Hlawacek, G.: HI+AS+BI+NS-WeM5, 27; HI+AS-TuA3, 16  
 Hmelo, A.B.: AS-TuP6, 20  
 Ho, W.: NS+AS-TuA8, 18  
 Hofmann, T.: EL+AS+EM+MS+PS+TF-FrM3, 45; EL+AS+EM+MS+PS+TF-FrM5, 45  
 Hogan, S.: AS-TuP22, 23  
 Holbrook, R.D.: BI+AS+NS+SS-WeA3, 31  
 Horn, M.W.: EL+AS+EM+MS+PS+TF-ThA10, 43  
 Hu, S.: IS+AS+SS-MoA8, 9  
 Hu, Y.F.: AS-WeA9, 31  
 Huang, L.: AS-WeA7, 30  
 Hurley, P.K.: AS-TuP17, 22  
 Hutton, S.J.: AS-MoM10, 3; AS-TuA7, 14; BI-ThM4, 35

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Ianno, N.: EL+AS+EM+MS+PS+TF-ThA8, 43  
 Ibuki, S.: AS-TuM10, 11  
 Ichiki, K.: AS-TuM10, 11  
 Iedema, M.J.: AS-ThM2, 34  
 Iijima, T.: HI+AS+BI+NS-WeM3, 26  
 Illas, F.: IS+AS+SS-MoM3, 4

Ishizaki, I.: AS-TuM11, 11  
 Itoh, H.: HI+AS+BI+NS-WeM12, 27  
 Ivanov, B.: AS-TuP6, 20  
 Iwasaki, T.: HI+AS+BI+NS-WeM12, 27  
 Iwaya, T.: AS+BI+NS-WeM5, 25

— J —

Jablin, M.S.: NT+AS+MI-WeM10, 29  
 Jablonski, A.: AS-MoM4, 2  
 Järrendahl, K.: EL+AS+EM+MS+PS+TF-ThM4, 37  
 Jarvis, J.D.: AS-TuP6, 20  
 Jaye, C.: AS-TuA3, 14  
 Jennings, G.K.: AS-ThM3, 34; BI+AS+NS+SS-WeA11, 33  
 Jensen, D.: AS-WeA11, 31  
 Jeon, S.: NS+AS-TuA1, 17  
 Jetter, R.: AS-ThM1, 34  
 Jiang, W.: AS-TuP15, 22  
 Johansson, N.: IS+AS+SS-MoM9, 5  
 Johnson, J.: IS-TuP3, 24  
 Johnson, M.D.: AS-MoM9, 3  
 Johnston, E.: BI-ThM9, 36  
 Johs, B.: EL+AS+EM+MS+PS+TF-FrM1, 45  
 Jones, E.M.: NT+AS-WeA8, 33  
 Joshi, S.M.: TC+AS+EM-ThM10, 39  
 Jung, S.J.: IS+AS+SS-TuM10, 13

— K —

Kacher, J.: IS+AS+SS-MoA1, 8  
 Kanyal, S.: AS-WeA11, 31  
 Karadge, M.: AS-WeA9, 31  
 Kariis, H.: EL+AS+EM+MS+PS+TF-ThM4, 37  
 Kaspar, T.C.: IS+AS+SS-MoM5, 4  
 Kasputis, T.: EL+AS+EM+MS+PS+TF-ThM5, 37  
 Kassan, S.: AS-MoA10, 7  
 Kathan-Galipeau, K.: AS+BI+NS-WeM9, 26  
 Kawai, M.: AS+BI+NS-WeM5, 25  
 Kazumi, H.: AS-ThM9, 35  
 Keating, P.L.: TR+AS+SS-ThM6, 40  
 Kemp, C.: AS-WeA8, 31  
 Kent, M.: NT+AS-WeA11, 33  
 Kent, T.: AS-TuP17, 22  
 Kersting, R.: AS-TuM9, 11  
 Kessels, W.M.M.: EL+AS+EM+MS+PS+TF-ThA7, 42; IS+AS+SS-MoA9, 9  
 Kholine, N.: AS-TuP5, 20  
 Kibelka, G.: AS-MoA10, 7  
 Kiefer, B.: AS-TuP3, 20  
 Kim, C.K.: AS-TuP18, 22  
 Kim, D.H.: IS+AS+SS-TuM10, 13  
 Kim, H.: TC+AS+EM-ThM1, 38  
 Kim, J.M.: TC+AS+EM-ThM1, 38  
 Kim, K.-J.: AS-TuP11, 21  
 Kim, S.: AS-TuA9, 15; IS+AS+SS-TuM10, 13; NS+AS-TuA1, 17  
 Kim, W.K.: TR+AS+SS-ThM4, 40  
 Kimura, Y.: AS-ThM9, 35  
 Kish, E.R.: IS+AS+SS-TuM12, 13  
 Kitzinger, L.: EL+AS+EM+MS+PS+TF-FrM7, 46; EL+AS+EM+MS+PS+TF-ThM10, 38  
 Klose, F.: NT+AS+MI-WeM3, 28  
 Knoops, H.C.M.: EL+AS+EM+MS+PS+TF-ThA7, 42; IS+AS+SS-MoA9, 9  
 Knudsen, J.: IS+AS+SS-MoM9, 5  
 Knutson, C.: AS-MoM9, 5  
 Kohler, J.L.: AS-TuP6, 20  
 Kompa, K.-L.: AS-MoA3, 6  
 Korolkov, V.V.: AS+BI+NS-WeM12, 26  
 Koster, N.B.: HI+AS-TuA12, 17  
 Koyama, H.: AS-ThM9, 35  
 Kreuzer, M.: NT+AS-WeA10, 33  
 Kroemker, B.: AS-MoM11, 3  
 Kubo, A.: AS-TuM11, 11  
 Kuchibhatla, S.V.N.T.: AS-TuP15, 22; AS-WeA7, 30  
 Kuhn, K.: AS-MoA10, 7  
 Kühne, P.: EL+AS+EM+MS+PS+TF-FrM3, 45; EL+AS+EM+MS+PS+TF-FrM5, 45  
 Kuk, Y.: NS+AS-TuA1, 17

Kummel, A.C.: AS-TuP17, 22; BI-ThM11, 36  
 Kung, P.: AS-TuA9, 15  
 Kutz, T.: BI-ThM12, 36  
 Kwong, H.M.: BI-ThM12, 36

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LaBella, V.P.: AS+BI+NS-WeM11, 26  
 Labuda, A.: TR+AS+SS-ThM1, 40  
 Lahouij, I.: TR+AS+SS-ThM10, 41  
 Lai, R.Y.: EL+AS+EM+MS+PS+TF-ThM6, 37  
 Laibinis, P.: BI+AS+NS+SS-WeA10, 32  
 Landin, J.: EL+AS+EM+MS+PS+TF-ThM4, 37  
 Langhammer, C.B.: BI+AS+NS+SS-WeA4, 32  
 Larson, P.E.: AS-ThM10, 35  
 Larsson, E.M.K.: BI+AS+NS+SS-WeA4, 32  
 Lauter, V.: NT+AS+MI-WeM3, 28; NT+AS+MI-WeM4, 28; NT+AS+MI-WeM5, 28  
 Laver, M.: NT+AS+MI-WeM5, 28  
 Lawrie, J.: BI+AS+NS+SS-WeA10, 32  
 Lea, A.S.: AS-ThM4, 34; AS-TuA1, 14  
 Lee, B.-J.: AS-MoA3, 6  
 Lee, J.: AS-TuP11, 21  
 Lee, J.L.S.: AS-MoA9, 7; AS-TuM4, 10  
 Lee, W.S.: TC+AS+EM-ThM1, 38  
 Lee, Y.: AS-TuP11, 21  
 Leggett, G.: BI+AS+NS+SS-WeA9, 32  
 Leick, N.: EL+AS+EM+MS+PS+TF-ThA7, 42  
 Leighton, C.: NT+AS+MI-WeM5, 28  
 Levi, D.: EL+AS+EM+MS+PS+TF-ThA1, 42  
 Lewis, T.: IS+AS+SS-TuM11, 13  
 Li, Q.: NS+AS-TuA7, 18; TR+AS+SS-ThM12, 41  
 Libuda, J.: IS+AS+SS-MoM3, 4  
 Licciardello, A.: AS-TuM4, 10  
 Lidzey, D.: BI+AS+NS+SS-WeA9, 32  
 Lim, W.C.: AS-TuP11, 21  
 Lin, Y.S.: AS-TuP22, 23  
 Linford, M.R.: AS-WeA11, 31  
 Liu, F.: AS-WeA7, 30  
 Liu, G.: IS+AS+SS-MoA1, 8  
 Liu, J.: TR+AS+SS-ThM6, 40  
 Liu, Y.: AS-MoA4, 6  
 Liu, Z.: IS+AS+SS-MoM4, 4; IS+AS+SS-TuM9, 12  
 Lloyd, K.G.: AS-WeA3, 30  
 Lohstreter, L.: AS-MoM3, 2  
 Lopez, G.P.: BI+AS+NS+SS-WeA9, 32  
 Lott, D.: NT+AS+MI-WeM3, 28  
 Louis, K.: BI+AS+NS+SS-WeA3, 31  
 Lowder, J.E.: IS+AS+SS-MoA6, 8  
 Lucatoro, T.B.: EL+AS+EM+MS+PS+TF-ThM9, 38  
 Lundgren, E.: IS+AS+SS-MoM4, 4; IS+AS+SS-MoM6, 4  
 Lykhach, Y.: IS+AS+SS-MoM3, 4  
 Lysaght, P.: AS-TuP20, 23

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Maas, D.J.: HI+AS-TuA12, 17; HI+AS-TuA4, 16  
 Machida, M.: NS+AS-TuA1, 17  
 Mack, P.: AS-TuA4, 14; AS-WeA2, 30  
 Mackus, A.J.M.: EL+AS+EM+MS+PS+TF-ThA7, 42; IS+AS+SS-MoA9, 9  
 Maier, M.: NS+AS-TuA11, 18  
 Majewski, J.: NT+AS+MI-WeM10, 29; NT+AS-WeA8, 33  
 Makino, H.: AS-ThM9, 35; TC+AS+EM-ThM2, 38  
 Maksymovych, P.: NS+AS-TuA7, 18  
 Mandelkow, E.: NT+AS-WeA8, 33  
 Mani-Gonzalez, P.G.: AS-TuP21, 23  
 Mankey, G.J.: NT+AS+MI-WeM3, 28  
 Marquis, Jr., J.P.: AS-TuP13, 21  
 Marsillac, S.: EL+AS+EM+MS+PS+TF-ThA4, 42  
 Mårtensson, N.: IS+AS+SS-MoM9, 5  
 Martin, J.M.: TR+AS+SS-ThM10, 41  
 Martin, N.M.: IS+AS+SS-MoM4, 4; IS+AS+SS-MoM6, 4  
 Martini, A.: TR+AS+SS-ThM12, 41  
 Marvel, R.E.: EL+AS+EM+MS+PS+TF-ThA11, 43



Master, E.R.: AS-MoA11, 7  
 Matolin, V.: IS+AS+SS-MoM3, 4  
 Matsuda, Y.: IS-TuP1, 24  
 Matsunaga, S.: AS+BI+NS-WeM5, 25  
 Matsuo, J.: AS-TuM10, **11**  
 Matthes, F.: NS+AS-TuA11, 18  
 McAllister, D.R.: AS-TuP13, 21  
 McAllister, N.M.: AS-TuP13, 21  
 McCarthy, J.: BI+AS+NS+SS-WeA3, 31  
 McDonnell, S.: IS+AS+SS-MoM10, **5**  
 Mejia, J.I.: TC+AS+EM-ThM11, 39  
 Melitz, W.: AS-TuP17, 22  
 Mendez, N.: BI-ThM11, **36**  
 Mendoza-Galvan, A.: AS-TuP21, 23  
 Merkle, A.P.: HI+AS-TuA3, 16  
 Messing, M.E.: IS+AS+SS-MoM4, 4  
 Messmer, B.T.: BI-ThM11, 36  
 Meyer III, H.M.: AS-TuP14, **22**  
 Migani, A.: IS+AS+SS-MoM3, 4  
 Milasinovic, S.: AS-MoA4, 6  
 Miller, J.: AS-MoA8, 7  
 Miller, M.: TR+AS+SS-ThM2, 40  
 Mims, C.A.: AS-MoA11, 7  
 Min, K.S.: AS-TuP18, 22  
 Min, Y.H.: IS+AS+SS-TuM10, **13**  
 Miro, H.: HI+AS-TuA10, 17  
 Miyayama, T.: AS-ThM11, 35; AS-TuM1, **10**  
 Mochizuki, Y.: AS-ThM9, 35  
 Moellers, R.: AS-TuM5, 10; AS-TuM9, **11**  
 Moffitt, C.E.: BI-ThM4, 35  
 Mönig, H.: NS+AS-TuA4, 17  
 Moore, J.F.: AS-MoA4, **6**  
 Morra, M.: AS-WeA9, 31  
 Moseley, M.W.: IS+AS+SS-MoA6, 8  
 Motyka, M.A.: EL+AS+EM+MS+PS+TF-ThA10, **43**  
 Moulder, J.: AS-ThM10, 35; AS-TuP4, 20  
 Mulders, A.: NT+AS+MI-WeM3, 28  
 Murphy, A.M.: BI-ThM12, 36

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Nachimuthu, P.: AS-ThM4, 34; AS-TuP15, 22  
 Nag, J.: EL+AS+EM+MS+PS+TF-ThA11, 43  
 Naik, R.R.: AS+BI+NS-WeM6, 25  
 Nam, T.W.: TC+AS+EM-ThM1, **38**  
 Nanayakkara, S.: AS+BI+NS-WeM10, 26  
 Nandasingh, M.L.: AS-TuP15, 22; AS-WeA7, 30  
 Narayanan, S.: TC+AS+EM-ThM9, **39**  
 Neyman, K.M.: IS+AS+SS-MoM3, 4  
 Niehuis, E.: AS-TuM5, 10; AS-TuM9, 11; AS-WeA1, 30  
 Notte, J.A.: HI+AS-TuA1, **15**; HI+AS-TuA3, 16  
 Ntwaaborwa, O.M.: AS-TuP23, **23**  
 Nunney, T.S.: AS-TuA2, **14**; AS-TuP8, 21

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Oertel, M.: NS+AS-TuA11, 18  
 Ogawa, S.: HI+AS+BI+NS-WeM3, **26**  
 Ogieglo, W.: EL+AS+EM+MS+PS+TF-ThA9, 43  
 Oh, J.S.: AS-TuP18, **22**  
 Oh, Y.: NS+AS-TuA1, 17  
 Ohashi, Y.: AS-TuM11, 11  
 Ohlhausen, J.: AS-MoA8, 7  
 Olsson, A.: IS+AS+SS-MoM9, 5  
 Onishi, K.: HI+AS+BI+NS-WeM12, 27  
 Orr, G.: HI+AS+BI+NS-WeM11, 27  
 Owen, J.H.G.: IS+AS+SS-MoM10, 5

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Pachuta, S.J.: AS-MoA7, **6**  
 Padmaperuma, A.B.: AS-ThM11, 35  
 Page, S.C.: BI-ThM4, 35  
 Pan, M.H.: NS+AS-TuA7, 18  
 Pan, X.: AS-TuP15, 22  
 Pannier, A.K.: EL+AS+EM+MS+PS+TF-ThM5, 37  
 Park, E.H.: IS+AS+SS-TuM10, 13  
 Park, J.: AS-TuP23, 23  
 Paul, D.F.: AS-TuP19, **22**  
 Peckys, D.B.: IS+AS+SS-TuM3, 12; IS+AS+SS-TuM5, **12**

Penzak, J.S.: AS-MoA4, 6  
 Perez, R.: NS+AS-TuA4, 17  
 Petrova, G.P.: IS+AS+SS-MoM3, 4  
 Phillips, M.C.: AS-TuA1, 14  
 Phillpot, S.R.: TR+AS+SS-ThM3, 40  
 Piao, H.: AS-WeA9, **31**  
 Piasecki, J.D.: AS-TuP13, 21; AS-TuP8, 21  
 Pickard, D.S.: HI+AS+BI+NS-WeM9, **27**  
 Piel, J.P.: EL+AS+EM+MS+PS+TF-FrM7, 46;  
 EL+AS+EM+MS+PS+TF-ThM10, 38  
 Pietzsch, A.: IS+AS+SS-MoM9, 5  
 Plasencia, A.: AS-TuP8, 21  
 Podraza, N.J.: EL+AS+EM+MS+PS+TF-ThA10, 43; EL+AS+EM+MS+PS+TF-ThA3, **42**  
 Poelsema, B.: HI+AS+BI+NS-WeM5, 27; HI+AS-TuA3, 16; IS+AS+SS-MoA7, **8**  
 Polikarpov, E.: AS-ThM11, 35  
 Ponnusamy, N.: AS-WeA7, 30  
 Porter, L.: AS-WeA7, 30; TC+AS+EM-ThM9, 39  
 Powell, C.J.: AS-MoM4, **2**  
 Prince, K.C.: IS+AS+SS-MoM3, 4  
 Prosa, T.: AS-WeA7, 30  
 Pruemper, G.: AS-MoM11, 3

— **Q** —

Quevedo-Lopez, M.A.: TC+AS+EM-ThM11, **39**

— **R** —

Rack, P.D.: HI+AS-TuA10, 17  
 Rading, D.: AS-TuM5, **10**; AS-TuM9, 11  
 Raman, S.N.: AS-ThM10, **35**  
 Randall, J.N.: IS+AS+SS-MoM10, 5  
 Ranjan, V.: EL+AS+EM+MS+PS+TF-ThA4, 42  
 Raschke, M.: AS-TuA1, 14  
 Ratner, B.D.: BP-SuA7, **1**  
 Rauch, S.: EL+AS+EM+MS+PS+TF-ThM3, **37**  
 Rayner, G.B.: TC+AS+EM-ThM6, 39  
 Reinhardt, M.: NT+AS-WeA10, 33  
 Remmert, J.L.: AS+BI+NS-WeM6, **25**  
 Resta, A.: IS+AS+SS-MoM6, 4  
 Richter, L.J.: EL+AS+EM+MS+PS+TF-ThM9, **38**  
 Richter, R.P.: AS-MoA1, **6**  
 Rignall, M.: AS-TuP2, 20  
 Rijnders, G.: IS+AS+SS-MoA3, **8**  
 Ritz, E.: TC+AS+EM-ThM6, **39**  
 Roberts, A.J.: AS-MoM10, 3; AS-TuA7, 14; BI-ThM4, 35  
 Roberts, C.J.: AS+BI+NS-WeM12, 26  
 Robertson, I.M.: IS+AS+SS-MoA1, **8**  
 Robinson, M.: AS-TuM6, 10  
 Rodenhausen, K.B.: EL+AS+EM+MS+PS+TF-ThM5, **37**; EL+AS+EM+MS+PS+TF-ThM6, 37  
 Rogers, B.R.: AS-ThM3, 34; AS-WeA10, **31**; BI+AS+NS+SS-WeA10, 32  
 Roozeboom, F.: IS+AS+SS-MoA9, 9  
 Rosenhahn, A.: IS+AS+SS-TuM6, 12  
 Rossi, F.J.: BI-ThM6, **36**  
 Ruidiaz, M.E.: BI-ThM11, 36  
 Ruzic, D.N.: TC+AS+EM-ThM6, 39  
 Ryan, K.E.: TR+AS+SS-ThM6, 40

— **S** —

Salas-Villasenor, A.: TC+AS+EM-ThM11, 39  
 Salditt, T.: IS+AS+SS-TuM6, 12  
 Salmeron, M.: IS+AS+SS-TuM1, 11  
 Salvati, L.: BI-ThM2, **35**  
 Sanada, N.: AS-TuM1, 10  
 Sanchez, A.B.: BI-ThM11, 36  
 Sanchez-Martinez, A.: AS-TuP20, 23  
 Sanderson, R.: AS-MoM3, 2  
 Sasaki, T.: TC+AS+EM-ThM2, 38  
 Schaff, W.J.: EL+AS+EM+MS+PS+TF-FrM3, 45  
 Schmalz, K.: NT+AS+MI-WeM3, 28  
 Schmidt, A.B.: NS+AS-TuA12, 19  
 Schmidt, D.: EL+AS+EM+MS+PS+TF-FrM4, **45**; EL+AS+EM+MS+PS+TF-FrM5, 45; EL+AS+EM+MS+PS+TF-ThA8, 43; EL+AS+EM+MS+PS+TF-ThM5, 37  
 Schmidt, W.: NT+AS+MI-WeM3, 28  
 Schmidt-Stein, F.: AS-TuP19, 22

Schmitt, J.: NT+AS+MI-WeM5, 28  
 Schmuki, P.: AS-TuP19, 22  
 Schnadt, J.: IS+AS+SS-MoM9, **5**  
 Schneider, C.M.: NS+AS-TuA11, 18  
 Schöche, S.: EL+AS+EM+MS+PS+TF-FrM3, **45**  
 Schönherr, H.: BI+AS+NS+SS-WeA7, **32**  
 Schreyer, A.: NT+AS+MI-WeM3, 28  
 Schroder, H.: AS-MoA3, 6  
 Schubert, E.: EL+AS+EM+MS+PS+TF-FrM4, 45; EL+AS+EM+MS+PS+TF-FrM5, 45; EL+AS+EM+MS+PS+TF-ThA8, 43  
 Schubert, M.: EL+AS+EM+MS+PS+TF-FrM3, 45; EL+AS+EM+MS+PS+TF-FrM4, 45; EL+AS+EM+MS+PS+TF-FrM5, 45; EL+AS+EM+MS+PS+TF-ThA8, **43**; EL+AS+EM+MS+PS+TF-ThM5, 37; EL+AS+EM+MS+PS+TF-ThM6, 37  
 Schwarz, U.D.: NS+AS-TuA4, 17  
 Schweikert, E.A.: BI+AS+NS+SS-WeA1, **31**  
 Schwendemann, T.C.: NS+AS-TuA4, 17  
 Schwoeble, A.J.: AS-TuP13, 21  
 Scipioni, L.: HI+AS-TuA1, 15; HI+AS-TuA3, 16  
 Seah, M.P.: AS-MoA9, 7  
 Seki, T.: AS-TuM10, 11  
 Sell, C.H.: BI-ThM12, 36  
 Sell, D.A.: BI-ThM12, 36  
 Senkbeil, T.: IS+AS+SS-TuM6, 12  
 Sezen, H.: AS-MoM6, **2**  
 Sgammato, W.: AS-TuP13, 21  
 Shan, T.-R.: TR+AS+SS-ThM3, **40**  
 Shard, A.G.: BP-SuA3, **1**  
 Sharma, M.: NT+AS+MI-WeM5, 28  
 Shavorskiy, A.: IS+AS+SS-TuM9, **12**  
 Shen, G.: AS-TuA9, 15  
 Shen, J.: AS-TuP17, 22  
 Shi, J.: EL+AS+EM+MS+PS+TF-FrM3, 45  
 Shibata, T.: TC+AS+EM-ThM2, 38  
 Shin, K.: AS-TuP11, 21  
 Shinada, H.: AS-ThM9, 35  
 Shinohara, M.: IS-TuP1, **24**  
 Shutthanandan, V.: AS-WeA7, 30; HI+AS+BI+NS-WeM11, 27  
 Siegbahn, H.: IS+AS+SS-MoM9, 5  
 Sinnott, S.B.: TR+AS+SS-ThM10, 41; TR+AS+SS-ThM3, 40  
 Skála, T.: IS+AS+SS-MoM3, 4  
 Skomski, R.: EL+AS+EM+MS+PS+TF-FrM5, 45  
 Smentkowski, V.S.: AS-TuP10, **21**  
 Smith, D.A.: HI+AS-TuA10, **17**  
 Srikanti, K.: NT+AS+MI-WeM9, **28**  
 Staib, P.G.: IS+AS+SS-MoA6, 8  
 Staudt, T.: IS+AS+SS-MoM3, 4  
 Steitz, R.: NT+AS-WeA10, 33  
 Stern, L.A.: HI+AS-TuA1, 15  
 Stickle, W.: AS-MoM9, **3**  
 Strobl, M.: NT+AS-WeA10, 33  
 Strohmeier, B.R.: AS-TuP13, **21**; AS-TuP8, 21  
 Suh, H.: NS+AS-TuA1, 17  
 Sullivan, E.: AS-TuA3, 14  
 Sun, X.: TR+AS+SS-ThM3, 40  
 Surman, D.J.: AS-MoM10, 3; BI-ThM4, 35  
 Sutter, P.: NS+AS-TuA10, 18  
 Suzer, S.: AS-MoM6, 2  
 Swart, H.C.: AS-TuP23, 23  
 Swensen, J.S.: AS-ThM11, 35  
 Szakal, C.: BI+AS+NS+SS-WeA3, **31**  
 Szulczewski, G.J.: NT+AS+MI-WeM4, 28

— **T** —

Takaki, Y.: IS-TuP1, 24  
 Takami, Y.: IS-TuP1, 24  
 Tarrico, C.: EL+AS+EM+MS+PS+TF-ThM9, 38  
 Tartakowskaya, E.: NT+AS+MI-WeM3, 28  
 Taubman, M.S.: AS-TuA1, 14  
 Tendler, S.J.B.: AS+BI+NS-WeM12, 26  
 Thevuthasan, S.: AS-TuP15, 22; AS-WeA7, 30  
 Thissen, A.: IS+AS+SS-MoA10, **9**  
 Thompson, G.B.: AS-TuA8, 15  
 Tilak, V.: AS-WeA9, 31  
 Tiwald, T.E.: EL+AS+EM+MS+PS+TF-FrM1, 45

Tizazu, G.: BI+AS+NS+SS-WeA9, 32  
 Todorovic, M.: NS+AS-TuA4, 17  
 Tolic, A.: HI+AS+BI+NS-WeM11, 27  
 Toomey, R.: NT+AS+MI-WeM10, 29  
 Torija, M.A.: NT+AS+MI-WeM5, 28  
 Tougaard, S.: AS-MoM1, 2  
 Trinchero, A.: IS+AS+SS-MoM6, 4  
 Tshabalala, K.G.: AS-TuP23, 23  
 Tsud, N.: IS+AS+SS-MoM3, 4  
 Tucker, R.T.: TC+AS+EM-ThM5, 39  
 Turchanin, A.: HI+AS+BI+NS-WeM6, 27  
 Turner, K.T.: TR+AS+SS-ThM6, 40  
 Tysoe, W.T.: TR+AS+SS-ThM9, 41

— **U** —

Uppireddi, K.: AS-TuP24, 23;  
 EL+AS+EM+MS+PS+TF-ThA6, 42

— **V** —

Vail, M.: AS-WeA11, 31  
 van der Drift, E.W.J.M.: HI+AS-TuA12, 17;  
 HI+AS-TuA4, 16  
 van Gastel, R.: HI+AS+BI+NS-WeM5, 27;  
 HI+AS-TuA3, 16; IS+AS+SS-MoA7, 8  
 van Langen, K.: HI+AS-TuA4, 16  
 van Veldhoven, E.: HI+AS-TuA12, 17; HI+AS-  
 TuA4, 16  
 Vandervorst: AS-TuA10, 15  
 Varela, M.: NT+AS+MI-WeM5, 28  
 Varga, T.: AS-TuP15, 22; AS-WeA7, 30  
 Vass, S.: BI-ThM2, 35  
 Vasudev, M.C.: AS+BI+NS-WeM6, 25  
 Vayssilov, G.N.: IS+AS+SS-MoM3, 4  
 Vazquez-Lepe, M.O.: AS-TuP20, 23; AS-TuP21,  
 23

Veligura, V.: HI+AS+BI+NS-WeM5, 27  
 Veyan, J.F.: IS+AS+SS-MoM10, 5  
 Vlasak, P.R.: AS-MoA7, 6  
 Voci, D.: HI+AS-TuA3, 16  
 Voevodin, A.A.: AS+BI+NS-WeM6, 25

— **W** —

Walker, A.R.: AS-TuP2, 20  
 Wallace, R.M.: IS+AS+SS-MoM10, 5  
 Walle, L.E.: IS+AS+SS-MoM4, 4  
 Walls, D.J.: AS-WeA3, 30  
 Wang, C.M.: AS-WeA7, 30  
 Wang, H.: EL+AS+EM+MS+PS+TF-ThM5, 37;  
 EL+AS+EM+MS+PS+TF-ThM6, 37  
 Wang, W.: AS-MoM9, 3  
 Weber, J.W.: EL+AS+EM+MS+PS+TF-ThA7, 42  
 Weber, M.J.: EL+AS+EM+MS+PS+TF-ThA7, 42  
 Wei, R.: TR+AS+SS-ThM2, 40  
 Wei, S.-H.: TC+AS+EM-ThM3, 39  
 Weidner, T.: AS-TuA3, 14  
 Weinert, M.: TR+AS+SS-ThM9, 41  
 Weiss, S.M.: BI+AS+NS+SS-WeA10, 32  
 White, R.G.: AS-WeA2, 30  
 Wilbert, S.: AS-TuA9, 15  
 Wilkens, B.J.: BI-ThM12, 36  
 Winkler, K.: AS-MoM11, 3  
 Winter, B.: IS+AS+SS-TuM11, 13  
 Woll, A.R.: IS+AS+SS-TuM12, 13  
 Wong, P.: AS-ThM1, 34  
 Woollam, J.A.: EL+AS+EM+MS+PS+TF-FrM3,  
 45; EL+AS+EM+MS+PS+TF-FrM5, 45  
 Wormeester, H.: EL+AS+EM+MS+PS+TF-ThA9,  
 43  
 Wright, A.E.: AS-TuA4, 14; AS-WeA2, 30  
 Wulff, K.: NS+AS-TuA12, 19

Wyre, J.P.: AS-WeA3, 30

— **X** —

Xiao, Z.: AS-WeA8, 31  
 Xie, Y.: HI+AS+BI+NS-WeM11, 27  
 Xu, Q.: IS+AS+SS-MoA8, 9

— **Y** —

Yamada, T.: AS+BI+NS-WeM5, 25  
 Yamamoto, A.: AS-TuM11, 11  
 Yamamoto, N.: TC+AS+EM-ThM2, 38  
 Yamamoto, T.: TC+AS+EM-ThM2, 38  
 Yamamoto, Y.: AS-TuM10, 11  
 Yamanobe, T.: AS-TuM10, 11  
 Yan, L.: AS-TuP24, 23;  
 EL+AS+EM+MS+PS+TF-ThA6, 42  
 Yang, L.: AS-ThM2, 34  
 Yeom, G.Y.: AS-TuP18, 22  
 Yip, C.: AS+BI+NS-WeM3, 25  
 Youn, Y.-S.: IS+AS+SS-TuM10, 13  
 Yu, X.: AS-ThM2, 34

— **Z** —

Zahl, P.: NS+AS-TuA10, 18  
 Zandvliet, H.: HI+AS+BI+NS-WeM5, 27; HI+AS-  
 TuA3, 16; IS+AS+SS-MoA7, 8  
 Zhang, L.: AS-WeA3, 30  
 Zhdanov, V.P.: BI+AS+NS+SS-WeA4, 32  
 Zhermenkov, M.: NT+AS+MI-WeM10, 29  
 Zhu, J.F.: IS+AS+SS-MoA8, 9  
 Zhu, Z.: AS-ThM2, 34; AS-ThM4, 34  
 Zoric, I.L.: BI+AS+NS+SS-WeA4, 32  
 Zou, M.: TR+AS+SS-ThM2, 40  
 Zulkifli, A.R.: BI+AS+NS+SS-WeA11, 33