Applied Surface Science
Room: 316 - Session AS+MC-MoM

Quantitative Surface Analysis
Moderator: James A. (Tony) Ohlhausen, Sandia National Laboratories, William Stickle, Hewlett Packard

8:20am **AS+MC-MoM1 Automating Multi-Technique Surface Analyses for Materials Characterisation**, ***Andrew Wright***, *P. Mack, T.S. Nunney, A. Bushell, A. Yeadon*, Thermo Fisher Scientific, UK

X-ray photoelectron spectroscopy (XPS) is a well-established technique that has become a cornerstone of surface analysis due to the wealth of chemical bonding information that it provides. Many other surface sensitive techniques exist, of course, and often can be found on the same instrumentation. Ultraviolet photoelectron spectroscopy (UPS) provides detailed valence electronic structure information. Reflection electron energy loss spectroscopy (REELS) can yield hydrogen quantification, shake-up transition and band gap information. Ion scattering spectroscopy (ISS) offers the most surface-sensitive probe of composition. Auger electron spectroscopy (AES) offers chemical information with high spatial resolution. In addition, monatomic and cluster ion beams can be used in concert with these methods for cleaning or depth profiling.

The various techniques can each provide important information in isolation, but the real power of surface analysis comes from combining these analyses of a sample and correlating the information to provide a more thorough characterisation of the material. Traditionally, however, switching between techniques has been difficult or laborious, and this has tended to deter analysts from performing multitechnique studies. Improvements to automation and usability are vital for bringing the less-used methods into common practice.

This paper presents several multitechnique surface analyses of samples in a single instrument (the Thermo Scientific Escalab250Xi) , showing how automated, sequential applications of these complementary chemical, electronic and structural characterisation methods can be applied to polymeric, catalyst, photovoltaic and semiconductor materials, yielding valuable results with minimal effort.

8:40am **AS+MC-MoM2 The *S'* component in the Si 2*p* X-ray Photoemission Spectrum of Si [001]**, ***Alberto Herrera-Gomez,*** CINVESTAV-Queretaro, Mexico, *M.O. Vazquez-Lepe,* Universidad de Guadalajara, Mexico, *P.G. Mani-Gonzalez,* Universidad Autónoma de Ciudad Juárez, Mexico, *O. Ceballos-Sanchez*, CINVESTAV-Queretaro, Mexico

Because of the technological relevance of the Si [001] surface, the Si 2*p* is one of the most studied core levels with laboratory X-Ray Photoelectron Spectroscopy (XPS). An important application is the quantification of the thickness of oxide layer, which is done by comparing the intensity of the substrate and Si^{4+} components. Peak-fitting is usually done by employing one doublet for the substrate and another for the Si^{4+} shifted around 3.5 or 4 eV to higher binding energy (from the substrate). In detailed studies, the quantification of the suboxides is usually done employing components, originally proposed by Himpsel et al.,[1] with the following shifts: 2.5 eV for Si^{3+}, 1.75 eV for Si^{2+}, and 0.95 eV for Si^{1+}. A proper fit, besides those five components, actually requires a six component shifted by approximately 0.3 eV. This peak has been clearly identified in various synchrotron studies such as that by Landemark et al.,[2] where it is referred as *S'*. In that study, and in others, it is assigned to one monolayer (the second) of the substrate. Although clearly present in Si 2*p* spectra obtained with laboratory XPS equipped with monochromatized Al Kα radiation, this component is largely unspoken in the literature. In one of the few studies that mention its existence it is assigned to an asymmetry of the bulk peak.[3] In this presentation it is going to be shown that this interpretation is inconsistent with the angular dependence observed by *S'*. The physical origin of *S'*, which is going to be discussed in detail, goes in a direction compatible with that proposed by Landemark et al.: although it represents one monolayer for the clean Si [001] surface, for oxide-covered surfaces it corresponds to a few monolayers of the substrate.

[1] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, and J. A. Yarmoff, Phys. Rev. B 38, 6084 (1998).

[2] E. Landemark, C. J. Karlsson, Y.-C. Chao, and R. I. G. Uhrberg, Phys. Rev. Lett. 60, 1588 (1992).

[3] D. F. Mitchell, K. B. Clark, J. A. Bardwell, W. N. Lennard, G. R. Massoumi and I. V. Mitchell. Surf. Inter. Anal. 21. 44-50 (1994).

9:00am **AS+MC-MoM3 Quantitative Analysis of Nanostructured Surfaces by means of X-ray Photoelectron Spectroscopy: Theory and Applications**, ***Wolfgang Werner***, Vienna University of Technology, Austria **INVITED**

The theory of signal emission in electron spectroscopy is discussed on the basis of the so-called Landau-Goudsmit-Saunderson (LGS) loss function, which leads in a natural way to rigorous spectrum analysis techniques, the so--called partial intensity analysis (PIA). Examples of applications include theoretical calculation of model spectra as well as analysis of experimental spectra using of X-ray Photoelectron Spectroscopy (XPS) and Reflection Electron Energy Loss Spectroscopy on nanostructured surfaces [1], the contribution of in-vacuo electron scattering to electron spectra [2] and secondary electron–electron energy loss coincidence spectroscopy (SE2ELCS) [3]. In the latter technique correlated electron pairs are analysed and detected, thereby giving unique insight into the dielectric properties of a solid.

A layered electron gas system will be considered as an important case study for quantitative surface analysis: it is shown how single layer graphene data can be extracted from measurements on macroscopic three dimensional highly oriented pyrolithic graphite (HOPG) samples. After appropriate analysis, a feature in the spectrum can be identified which quantitatively correlates with the sp2-content in arbitrary carbon samples, as follows from comparison with Raman measurements.

[1] W S M Werner, Surf. Interf. Anal. 31(2001)141

[2] Werner, Wolfgang S. M., Novak, Mihaly, Salvat-Pujol, Francesc, Jiricek, Petr, Zemek, Josef, PRL 110(2013)086110

[3] W. S. M. Werner, F. Salvat-Pujol, A. Bellissimo, R. Khalid, W. Smekal, M. Novak A. Ruocco and G. Stefani, Phys. Rev. B 88(2013)201407

9:40am **AS+MC-MoM5 Effective Attenuation Lengths for Hard X-ray Photoelectron Spectroscopy (HAXPES)**, *A. Jablonski,* Polish Academy of Sciences, Poland, ***Cedric Powell***, National Institute of Standards and Technology (NIST), *S. Tanuma*, National Institute for Materials Science (NIMS), Japan

HAXPES is now being used to characterize thicker overlayer films than is possible with conventional XPS using Al and Mg Kα x-ray sources. As a result, there is a need for effective attenuation lengths (EALs) to determine film thicknesses at electron energies larger than about 1.5 keV. Jablonski and Powell [1] published a simple practical EAL expression from fits to EALs calculated from solution of the kinetic Boltzmann equation within the transport approximation for electron energies between 61 eV and 2 keV and photoelectron emission angles between 0° and 50°. This approach has now been extended to electron energies up to 5 keV with account also taken of non-dipole terms in the photoionization cross section. EALs have been calculated for Si 1s, Cu $2p_{3/2}$, Ag $3d_{5/2}$, and Au $4f_{7/2}$ photoelectrons excited by Mg Kα, Al Kα, Zr Lα, and Ti Kα x rays using the inelastic mean free paths of Tanuma *et al*. [2] for each solid. EALs from the non-dipole approximation were up to about 2% larger than those from the dipole approximation. Good agreement has been found between the new EALs and EALs determined from Monte Carlo simulations and from the NIST SESSA database [3]; with the latter database, simulations can be made for photoelectron energies up to 20 keV. We found that the new EALs were also consistent with the previous expression [1]. Finally, the new EALs are reasonably consistent with the EALs measured by Sacchi e*t al*. [4] for Co, Cu, and Ge but there was poorer agreement with the EALs measured by Rubio-Zuazo and Castro [5] for Au. Disagreements between the calculated and measured EALs for Au at energies less than 5 keV were attributed to non-ideal morphologies of the thinner Au films.

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

[2] S. Tanuma, C. J. Powell, and D. R. Penn, Surf. Interface Anal. 43, 689 (2011).

[3] http://www.nist.gov/srd/nist100.cfm.

[4] M. Sacchi *et al*., Phys. Rev. B 71, 155117 (2005).

[5] J. Rubio-Zuazo and G. R. Castro, J. Electron Sprectrosc. Relat. Phenom. 184, 384 (2011).

10:00am **AS+MC-MoM6 Angle-Resolved XPS Test Structures Fabricated *In Situ* by Argon Ion and Argon Cluster Ion Treatment**, ***Peter Cumpson***, *A.J. Barlow, J.F. Portoles, N. Sano*, Newcastle University, UK

Nondestructive depth-profiling by inversion of Angle Resolved XPS spectra[1] has been a desire in the XPS community for a long time. The lack of reference specimens with known structures has been a severe handicap in

the development of the technique. Until now, reference materials with known depth-profiles have largely been confined to thin oxide layers on aluminium or silicon, and even these have uncertain carbon contamination layers. Progress has been made, though, with depth-profiling numerical methods[2] that need comparison with real known structures. It is difficult to fabricate structures with nanometre-scale variation in concentration with depth, and even more difficult to transport them without contamination (and the potentially damaging removal of such contamination).

We have developed protocols for the fabrication of two different samples, one organic and the other inorganic, with known depth-profiles *in situ* in XPS instruments;

Glancing-angle monatomic argon sputtered PEDOT:PSS, a common conducting polymer blend, and

Argon cluster-ion sputtered indium arsenide (InAs), a compound semiconductor

Indium arsenide and PEDOT:PSS are both widely-available, almost atomically flat and sufficiently electrically conductive to ensure no sample charging occurs. Glancing angle monatomic sputtering of PEDOT:PSS leaves a PEDOT enhanced region at the surface, the spatial parameters of which depend only on sputter ion conditions under direct experimental control. Recently we have demonstrated the unexpected result that argon gas-cluster sputtering of InAs results in a thin, coherent metallic indium layer at the surface[3], the basis for InAs reference material structure.

The ill-posed nature of the inversion of ARXPS data means it is sensitive to small experimental uncertainties. We apply three different ARXPS algorithms, including regularization, to the data from these in situ reference structures. This gives a set of reference data that will allow comparison with results from any XPS work following the same preparation protocol. This should greatly improve confidence in the results of ARXPS depth-profiling.

[1] P J Cumpson, Angle-resolved XPS and AES: depth-resolution limits and a general comparison of properties of depth-profile reconstruction methods, J Electron Spectrosc. and Rel. Phenom. 73 (1995) 25-52.

[2] R W Paynter, Regularization methods for the extraction of depth profiles from simulated ARXPS data derived from overlayer/substrate models, J Electron Spectrosc. and Rel. Phenom. 184 (2012) 569–582.

[3] A J Barlow and P J Cumpson, Observed damage during Argon gas cluster depth profiles of compound semiconductors, submitted to J Appl. Phys.

10:40am **AS+MC-MoM8 Metrology for Surface Chemical Analysis: Active Parties, Status and Challenges**, ***Wolfgang Unger***, BAM Federal Institute for Materials Research and Testing, Germany

The International Bureau of Weights and Measures (BIPM) defines metrology, i.e. the *Art of Measurement*, as "the science of measurement, embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology." Besides the establishment of full uncertainty budgets traceability is another aspect of metrology.

Surface chemical analysis is a much younger discipline in comparison to other branches in analytical chemistry as, e.g., electro-chemistry, inorganic and gas analysis and lots of work has to be done to make XPS, AES and SIMS based quantitative analysis a metrological one. Looking to the analytical methods established in surface chemical analysis we may differentiate classes:

1. Primary methods measuring amount of substance as [atoms/cm^2, …]

2. Empirical methods measuring amount of substance after calibration as fractions of a nano scaled surface layer

3. Primary and empirical methods measuring amount of substance expressed as the thickness of a thin film [nm]

In most cases we are using empirical methods when XPS, AES and SIMS are applied to deliver quantitative data. It follows also from that list that, principally, traceability to the mol or the meter can be established.

Relevant initiatives to metrologically underpin surface chemical analysis have been launched under the umbrella of the Surface Analysis Working Group at CCQM/BIPM where the National Metrology Institutes are running world-wide inter-laboratory comparisons. In Europe we have the European Metrology Research Program (EMRP) where a number of projects directly address issues of surface chemical analysis and most often also by individual websites. Another aspect is that there is a strong impact of metrology in surface chemical analysis on standardization in ISO TC 201 and 202. For example, ISO 14701 has been prepared using outcome of a huge key comparison organized under CCQM/BIPM.

The talk will present some basics of metrology in surface chemical analysis, results of successful key comparisons organized under CCQM/BIPM and a survey on the main scientific challenges to be addressed in quantitative surface chemical analysis in the next future.

11:00am **AS+MC-MoM9 Local Crystallography: Phases, Symmetries, and Defects from Bottom Up**, *A. Belianinov, Q. He, A,. Borisevich, S. Jesse, **Sergei Kalinin***, Oak Ridge National Laboratory

Progress in high-resolution real space imaging techniques such as (Scanning) Transmission Electron Microscopy (STEM) and Scanning Tunneling Microscopy (STM) has allowed high veracity, direct imaging of atomic columns (STEM) and surface atomic structures. While the data acquisition platforms are continuously evolving, the basic data processing principle - analysis of structure factor, or equivalently two point correlation function averaged over probing volume – remained invariant since the early days of Braggs. We propose an approach based on the multivariate statistical analysis of the coordination spheres of individual atoms to reveal preferential structures and symmetries. The underlying mechanism is that for each atom, *i*, laying on the lattice site with indices (*l, m*), we construct a near coordination sphere as a vector $\mathbf{N}_i = (x_1,..., x_8)$, where $(x_j, y_{j+1})$is the radius-vector to *j/2*-th nearest neighbor. Once the set of $\mathbf{N}_i$ vectors is assembled, its statistical properties are analyzed though cluster analysis and various multivariate methods to reveal and extract regions of symmetry, distortions, different phases, boundaries, defects, etc. Results are presented on various model and real material systems including $La_{0.7}Sr_{0.3}MnO_3$, $BiFeO_3$, $LaCoO_3$ and discussed in light of physical parameter extraction.

Acknowledgement:

Research for (AB, QH, AB, SJ, SVK) was supported by the US Department of Energy, Basic Energy Sciences, Materials Sciences and Engineering Division. Research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy.

11:20am **AS+MC-MoM10 Chemical Warfare Agent Surface Adsorption: Hydrogen Bonding of Sarin and Soman to Amorphous Silica**, ***Erin Durke**, W.O. Gordon,* Edgewood Chemical Biological Center, *A.R. Wilmsmeyer,* Augustana College, *D. Troya, J.R. Morris*, Virginia Tech

Sarin and soman are warfare nerve agents that represent some of the most toxic compounds ever synthesized. The extreme risk in handling such molecules has, until now, precluded detailed research into the surface chemistry of agents. We have developed a surface science approach to explore the fundamental nature of hydrogen bonding forces between these agents and a hydroxylated surface. Sarin and soman are deposited via a directional doser onto an amorphous silica surface and characterized by reflection-absorption infrared spectroscopy (RAIRS) in an ultra-high vacuum (UHV) chamber. Once the chemical agent coverage reached monolayer values, temperature programmed desorption is performed to determine the binding energy. Changes in the OH region of the IR spectra are monitored in real time with RAIRS, and the degree of shift in the H-bonded OH peak shows a linear relationship with the strength of the interaction between agent and silica surface. Infrared spectroscopy revealed that both agents adsorb to amorphous silica through the formation of surprisingly strong hydrogen-bonding interactions with primarily isolated silanol groups (SiOH). Comparisons with previous theoretical results reveal that this bonding occurs almost exclusively through the phosphoryl oxygen (P=O) of the agent. Temperature-programmed desorption experiments determined that the activation energy for hydrogen bond rupture and desorption of sarin and soman was 50 ± 2 kJ/mol and 52 ± 2 kJ/mol, respectively. X-ray photoelectron spectroscopy (XPS) is also used to confirm molecular desorption of the agents from the silica substrate. Together with results from previous studies involving other phosphoryl-containing molecules, we have constructed a detailed understanding of the structure-function relationship for nerve agent hydrogen bonding at the gas-surface interface.

11:40am **AS+MC-MoM11 The Shake-up Satellites in the Fe 2*p* Core Level X-ray Photoelectron Spectra Analyzed with the Double Lorentzian Line Shape**, ***M. Bravo-Sanchez,*** CINVESTAV-Queretaro, Mexico, *J.A. Huerta-Ruelas,* Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, Mexico, *A. Herrera-Gomez,* CINVESTAV-Queretaro, Mexico, *M.O. Vazquez-Lepe,* Universidad de Guadalajara, Mexico, *F. Espinosa-Magaña*, CIMAV-Unidad Chihuahua, Mexico

Within the transition metal oxides, Fe oxides are among the most technologically relevant. Surfaces analysis through techniques such as X-ray photoelectron spectroscopy (XPS) plays a crucial role in the development of new applications. Despite that a considerable effort has been made on Fe oxides with XPS, many questions are still unanswered mainly due to the lack of a simple and standardized method to adequately model the spectrum of the Fe 2*p* core level. Complex characteristics such as a steeply background, shake-up satellites, and an asymmetrical line-shape, have been the principal obstacle to obtain accurate areas for proper quantification. In this work, this problem has been confronted by employing the SVSC background [1] and the double Lorentzian line shape [2]. The

latter has many advantages over the traditionally employed Doniach-Sunjic line shape, since it is integrable and, then, suitable for quantitative studies.

With this combination of methods it has been possible to closely model the entire Fe 2*p* spectra (including both the 3/2 and 1/2 branches), which implied accounting for the shake-up satellite already known and the inclusion of a second satellite rarely reported in the literature. A proper determination of areas for accurate quantification of composition and thickness has been achieved taking into account this second satellite located around 725 eV (binding energy), hidden under the 1/2 branch of the main oxide peak. The inclusion of this second signal, together with the already known satellite, improves notably the quantitative analysis of the Fe oxides spectra. The position of the satellites shows a clear dependence on the oxide thickness. Thickness assessment has been confirmed with high-resolution transmission electron microscopy.

[1] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, and M.O. Vazquez-Lepe. Journal of Electron Spectroscopy and Related Phenomena (in press) DOI 10.1002/sia.5453.

[2] A. Herrera-Gomez. "A double Lorentzian shape for asymmetric photoelectron peaks." Internal Report. Cinvestav-Querétaro.(2011). http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 313 - Session MC+AP+AS-MoM

Characterization of 3D Structures, 2D films and Interconnects
Moderator: Paul Ronsheim, CTO, PAR Technical Consulting, previously with IBM, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

8:20am **MC+AP+AS-MoM1 Dopant/Carrier and Compositional Profiling for 3D-Structures and Confined Volumes.**, ***Wilfried Vandervorst***, *A. Kumar, J. Demeulemeester, A. Franquet, P. Eyben, J. Bogdanowicz, M. Mannarino, A. Kambham, U. Celano*, IMEC, KU Leuven Belgium **INVITED**

The introduction of three-dimensional devices (FinFets, TFETs and nanowires), has created as new metrology challenges the characterization of dopant /carrier and impurity distributions in 3D-devices and confined volumes. Beyond these dimensional challenges, the use of alternative materials such SiGe, Ge, GeSn alloys as well as III-V materials, adds to the metrology requirements. Recent evolution towards growth (and strain relaxation) mediated by the confined volume (for instance relying on aspect ratio trapping) calls for metrology suited for very small volumes and more atomic scale observations. Metrology in 3D-structures and confined volumes has demonstrated that the changing surface/volume ratios in confined devices versus blanket films lead to phenomena (dopant deactivation, enhanced diffusion,..) which cannot be observed in blanket experiments. Hence more emphasis should be placed on the analysis of device and structures with relevant dimensions relative to the exploration of blanket experiments.

Atomprobe tomography is able to provide composition analysis within very small volumes (a few nm3) with high sensitivity and accuracy and excellent spatial resolution. Hence this enables to observe dopant atom migration in 3D-devices, and through some data mining analysis, even cluster formation as precursor to strain relaxation such as seen in metastable alloys like GeSn. Field Ion Microscopy, a complement to APT, can be used to image impurity atoms clustered around defects within the crystal. Routine application of APT is still hampered by localization problems, reconstruction artifacts due to inhomogeneous evaporation, local magnification effects, sensitivity due to the limited statistics, laser-tip interaction phenomena, etc.

Although scanning spreading resistance microscopy is inherently 2D, analysis of 3D-devices (FinFet, ReRam, Sonos..) is possible by novel approaches such as SPM scalping. The introduction of novel modes such as soft retrace, FFT-SSRM has led of improved resolution and eliminates series resistances resulting from the current confinement in these narrow devices, decoupling the actual "spreading resistance" from the total resistance. Finally SSRM-carrier distribution have been coupled to device simulators leading to an accurate prediction of device performance.

In addition to APT we also present here the concept of "self focusing SIMS" whereby we demonstrate that it is possible to determine, for instance, the SiGe(III-V) composition in trenches as small as 20 nm without having an ion beam with nm-resolution. This represents a significant step forward in terms of production control and statistical relevance.

9:00am **MC+AP+AS-MoM3 Characterization of the Periodicity (Pitch) and Stress of Transistor Fin Structures using X-Ray Diffraction Reciprocal Space Mapping**, ***Alain Diebold***, *M. Medikonda,* SUNY College of Nanoscale Science and Engineering, *M. Wormington*, Jordan Valley Semiconductors Inc

Cleanroom compatible, high resolution X-Ray diffraction systems are now capable of measuring the average pitch and critical dimensions of ordered arrays of fins and the stress state of high mobility layers at the top of the fins. Reciprocal Space Mapping (RSM) characterizes both the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity. The periodicity of the fin arrays has decreased to the point where the fin array adds satellite diffraction peaks to the main Bragg diffraction peak from the semiconductor. The pitch can be calculated from the angular spacing of the satellite peaks. State of the art lithographic processing using the spacer patterning process often results in a different spacing between every other fin. This is known as pitch walking. Pitch walking is very difficult to observed, even using TEM cross-sectional images. The stress state of the high mobility epilayers such as $Si_{1-x}Ge_x$ on Si fins can also be characterized using RSMs. In addition, some of the higher order satellite peaks will split when the fins have a near rectangular shape. This presentation compares the capability of cleanroom and synchrotron based XRD systems for reciprocal space mapping of Si and $Si_{1-x}Ge_x$ / Si transistor fins arrays.[1]

[1] Measurement of Periodicity and Strain in Arrays of Single Crystal Silicon and Pseudomorphic $Si_{1-x}Ge_x$/Si Fin Structures using X-ray Reciprocal Space Maps, M. Medikonda, G. Muthinti, J. Fronheiser, V. Kamineni, M. Wormington, K. Matney, T. Adam, E. Karapetrovaand A.C. Diebold, J. Vac. Sci. Technol**. B32**, (2014), 021804.

9:20am **MC+AP+AS-MoM4 MBE Grading Techniques for the Growth of InAsSb Films with Inherent Properties Unaffected by Strain**, ***Wendy Sarney***, *S.P. Svensson,* US Army Research Laboratory, *Y. Lin, D. Wang, L. Shterengas, D. Donetsky, G. Belenky*, Stony Brook University

By using compositionally graded buffer layers, InAsSb can be grown by molecular beam epitaxy with its inherent lattice properties across the entire composition range. This direct bandgap, III-V alloy is of great interest for infrared detector applications, as it can cover both the mid (3-5 µm) and long wavelength (8-12 µm) bands. The direct bandgap provides the high quantum efficiency that allows it to directly compete with HgCdTe but at potentially much reduced fabrication costs. InAsSb was sidelined for decades, because conventional wisdom indicated its bandgap bowing parameter would not allow it to reach the needed 10-12 µm benchmark. The material was further maligned because it was thought to exhibit CuPt ordering, which affects the bandgap. By revisiting the growth techniques we have determined that the bandgap bowing parameter of InAsSb is more than sufficient for LWIR applications and it can be grown free of ordering, provided that the material is grown with its inherent, undistorted lattice constant.

As there is no perfect substrate available for the InAsSb compositions of interest (typically containing ~40-50% Sb), we grow the films on compositionally graded buffer layers on GaSb substrates. The buffer layers consist of AlGaInSb, GaInSb, or InAsSb grades based on the theories described by J. Tersoff.[1] In this paper we provide experimental verification of Tersoff's theories applied to ternary and quaternary grades, and for both tensile and compressive grades. Furthermore, the specific parameters calculated by Tersoff, such as the boundary for the dislocation-free region (Zc) is exactly verified by transmission electron microscopy (TEM).

Reciprocal space maps show that the InAsSb layers grown on compositional graded buffer layers have their native lattice constant. The films are free from strain-relieving dislocations within the field of view allowed by TEM. Furthermore, we see no evidence of group V ordering for films grown in this manner. Although ordering is known to further reduce the bandgap, it is a difficult property to control, and it would be very undesirable to rely on it to induce the needed longer wavelengths. We have observed that a finite amount of residual strain that is small enough not to cause dislocation formation can induce CuPt ordering, but this can be completely avoided by using appropriate grading techniques. We also see no evidence of phase segregation or miscibility gaps.

Photoluminescence wavelengths have been measured for numerous InAsSb films, with a maximum wavelength to date of 12.4 µm. This may be the ideal material for direct bandgap infrared device applications.

J. Tersoff, Appl. Phys. Lett. 62, 693 (1993);

9:40am **MC+AP+AS-MoM5 Quantitative 3-D Imaging of Filaments in Hybrid Resistive Memory Devices by Combined XPS and ToF-SIMS Spectroscopies**, *Y. Busby, **Jean-Jacques Pireaux***, University of Namur, Belgium

Resistive switching has been observed in a multitude of inorganic (oxides, chalcogenides...) and hybrid (organic or polymers plus metal nanoparticles) thin films simply sandwiched between two metal electrodes. Organic memory devices are particularly promising candidates for developing large scale, high density, cost efficient, non-volatile resistive memories. Their switching mechanism has been for a long time suggested to depend on the formation/rupture of localized conducting paths (filaments). Using electrical characterization by impedance spectroscopy, filament formation has been experimentally demonstrated to be the dominant switching mechanism in many organic memories, only very recently (2014). Otherwise, despite of very dedicated efforts, few experimental techniques have so far succeeded in characterizing and providing information on filament(s).

The present work combines for the first time High Resolution X-Ray induced Photoelectron Spectroscopy (for its quantitative information capability) and Time-of-Flight Secondary Ion Mass Spectrometry (for its very high atomic sensitivity and 3D imaging capabilities) to quantitatively study both lateral and in depth elements distribution in a complete and operative organic memory device: what happens to be top electrode metal diffusion and filament formation is evidenced and quantitatively evaluated in memory devices which are based on a highly insulating and *cross-linked polystyrene layer*, processed by plasma polymerization, sandwiched between silver and indium tin oxide electrodes. Depth profiles evidence the metal diffusion in pristine and electrically addressed memory elements through the whole organic layer where the silver concentration can reach value as high as 5.10^{19} at/cm^3. Filament formation is shown to be initiated during the top electrode evaporation, and is then successively enhanced by field induced diffusion during the electrical addressing. The 3-D ToF-SIMS images evidenced the formation of metallic paths extending through the entire device depth, electrically bridging the two electrodes when the element is in its low resistance state. Filaments with different characteristics have also been studied in organic memories based on a semiconducting polymer (Polyera N1400 ActiveInk) or on semiconducting small molecules (Tris-(8-hydroxyquinoline)aluminum, AlQ_3). It appears therefore that metallic filaments are indeed at the origin of switching in organic memory devices.

10:00am **MC+AP+AS-MoM6 High Throughput Electron Diffraction-Based Metrology of Nanocrystalline Materials**, *X. Liu,* Carnegie Mellon University*, D. Choi,* Korea Railroad Research Institute, Republic of Korea*, N.T. Nuhfer,* Carnegie Mellon University*, D.L. Yates, T. Sun,* University of Central Florida*, G.S. Rohrer,* Carnegie Mellon University*, K.R. Coffey,* University of Central Florida*, **Katayun Barmak***, Columbia University

The resistivity of Cu, the current interconnect material of choice, increases dramatically as the conductor's dimensions decrease towards and below the mean free path of electrons (39 nm at the room temperature). Two scattering mechanisms that contribute to this resistivity size effect are surface scattering, evidenced by thickness dependence of resistivity, and grain boundary scattering, evidenced by grain size dependence of resistivity. Quantification of microstructural parameters, such as grain size, at the scale of the resistivity size effect necessitates the use of transmission electron microscopy (TEM). In this work, an electron diffraction-based orientation mapping system installed on the TEM is used to characterize not only nanometric Cu films, but also new materials, W, Ni, Ru and Co, that are potential candidates to replace Cu as the next-generation interconnect material. In this characterization technique, spot diffraction patterns are collected as the nano-sized beam scans the area of interest. The crystallographic orientation of each scanned pixel is determined by cross-correlation with pre-calculated diffraction patterns (termed, templates). Precession is used to reduce the dynamical scattering effects, increasing the reliability of the orientation mapping. The raw orientation data is then processed to yield the microstructural data via a well-defined procedure developed to parallel that used to process electron backscatter orientation data taken in scanning electron microscopes. This characterization yields full range of microstructural parameters including grain size, grain size distribution, orientation distribution, misorientation distribution, grain boundary and interface character and plane distribution that are extracted from the crystal orientation maps in a nearly fully-automated manner. These microstructural parameters, along with sample thicknesses, are used to evaluate the validity of the semiclassical resistivity size models for Cu and the new materials, and, where applicable, to determine the relative contributions of surface and grain boundary scattering to the resistivity increase.

10:40am **MC+AP+AS-MoM8 LEIS Characterization of the Outer Surface, Ultra-Thin Layers and Contacts**, ***Hidde Brongersma**,* ION-TOF / Tascon / Calipso, Netherlands*, P. Bruener, T. Grehl,* ION-TOF GmbH, Germany*, H.R.J. ter Veen*, Tascon GmbH, Germany **INVITED**

Modern day technologies are increasingly based on high performance nanomaterials and novel preparation techniques for such materials are developed at a rapid pace. Advances in nanoscience and nanotechnology heavily rely on the availability of analytic techniques that can validate and support new nanomaterials synthesis procedures. With the introducing of the Qtac^{100}, a new high-sensitivity Low Energy Ion Scattering (HS-LEIS) instrument, one can quantitatively analyze the atomic composition of the surface of a wide range of materials with an unparalleled surface sensitivity.

The outermost atoms of a surface largely control processes such as growth, nucleation, poisoning, adhesion and electron emission. While analytic tools (such as XPS) probe an average of many atomic layers, LEIS can selectively analyze the outer atoms. In addition, non-destructive in-depth information, with high depth resolution, is obtained for the heavier elements (0 - 10 nm). HS-LEIS is just as well suited for the *quantitative analysis* of amorphous, insulating and extremely rough surfaces as for flat single crystals. Since HS-LEIS is a fast analysis technique, it can be used to follow diffusion processes in-situ.

The focus will be on applications where valuable information has been obtained that is impossible (or very difficult) to obtain with other analytical techniques. The unique possibilities will be illustrated with state-of-the-art applications for: ALD growth of ultra-thin layers, surface modification, interface diffusion, core/shell nanoparticles, graphene, self-assembled monolayers for sensors.

The findings will be compared and contrasted to those obtained by other analytic techniques such as XPS, Auger, SIMS, RBS and conventional LEIS.

11:20am **MC+AP+AS-MoM10 Backside versus Frontside Characterization of High-k/Metal Gate Stacks for CMOS sub-14 nm Technological Nodes**, ***Eugenie Martinez**,* CEA, LETI, MINATEC Campus, France*, B. Saidi, P. Caubet, F. Piallat,* STMicroelectronics, France*, H. Kim,* CEA, LETI, MINATEC Campus, France*, S. Schamm-Chardon,* CEMES-CNRS, France*, R. Gassilloud*, CEA, LETI, MINATEC Campus, France

Down-scaling of CMOS transistors beyond the 14 nm technological node requires the implementation of new architectures and materials. The gate last integration scheme is a promising solution to better control the threshold voltage of future MOSFETs, because of its low thermal budget [1]. Advanced characterization methods are needed to gain information about the chemical composition of such structures. The analysis of thin layers and interfaces buried under a thick metal electrode is particularly challenging. An effective approach based on backside sample preparation is proposed here.

To tune the work-function toward nMOS values, the technology currently investigated is based on HfO_2 for the dielectric and a thin TiN layer capped by a TiAl alloy for the gate [2]. For a better understanding of aluminium and other elements redistributions after a 400°C annealing, a specific methodology has been developed based on the removal of the Si substrate. It allows to achieve XPS and Auger analyses from the backside of the sample [3].

In particular, Auger depth profiling performed on HfO_2/TiN/TiAl/TiN/W gate stacks at low energy (500 eV Ar^+) brought the following main conclusions: a) no Al diffusion toward the HfO_2/TiN interface, b) nitrogen out diffusion in the upper TiAl film, c) significant oxygen scavenging. By comparison, these results evidenced that Auger frontside analyses suffer from sputter-induced artifacts.

In a further study, to understand the behavior of nitrogen out diffusion in the TiAl layer, we deposited $TiAlN_x$ thin films with various nitrogen flows by reactive sputtering deposition and performed backside XPS analyses. At low/medium nitrogen flows, which correspond to the $TiAlN_x$ film after TiN/TiAl bilayer anneal, the N1s core level spectra obviously shows that N is mainly bonded to Al rather than Ti. Results are compared with frontside XPS performed with a thinner TiN upper layer. The backside approach is shown to be more representative of the technological stack, in particular with respect to the TiN oxidation.

Measurements were carried out at the NanoCharacterization Platform (PFNC) of MINATEC.

[1] C. L. Hinkle et al., Appl. Phys. Let. 100, 153501 (2012).

[2] A. Veloso et al.., Symposium on VLSI Technology, Digest of Technical Papers (2011).

[3] M. Py et al., AIP conference proceedings 1395, 171 (2011).

11:40am **MC+AP+AS-MoM11 Charge Storage Properties of Al/(1-x)$BaTiO_{3-x}Ba(Cu_{1/3}Nb_{2/3})O_3$ (x = 0.025) (BTBCN)/HfO_2/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices**, ***Souvik Kundu***, *M. Clavel, D. Maurya, M. Hudait, S. Priya*, Virginia Tech

Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed laser deposited 300 nm (1-x)$BaTiO_{3-x}Ba(Cu_{1/3}Nb_{2/3})O_3$ (x = 0.025) (BTBCN) ferroelectric film and atomic layer deposited 10 nm HfO_2 insulating layer on silicon semiconductor substrate were developed for next generation ferroelectric non-volatile memory applications. For the first time, the structural, interfacial, and electrical properties of these Al/BTBCN/HfO_2/p-Si MFIS devices were studied, and the role of BTBCN as charge storing elements was also established. The X-ray diffraction and transmission electron micrograph with selected area diffraction pattern clearly demonstrate the single crystallization of BTBCN ferroelectric films. It was found that insertion of 10 nm HfO_2 in-between BTBCN and Si improves the interfacial properties and also prevents the interdiffusion of semiconductor into the ferroelectric layer. The optical bandgap of BTBCN was found to be 4.38 eV using transmission spectrum analysis. The MFIS structure showed capacitance-voltage hysteresis loops due to the ferroelectric polarization of BTBCN and the maximum memory window was found to be 1.65 V when the sweeping voltage was ±10 V. However, no memory window was found in metal-insulator-semiconductor devices, i.e., when there is no BTBCN layer in between metal and insulating layer. The leakage current of these devices was found to be 7×10^{-9} A/cm^2 at an applied voltage of -1 V. The wide memory window and superior retention properties were achieved due to the presence of BTBCN. The electronic band diagrams of these MFIS devices during program and erase operations were proposed.

Keywords: BTBCN; MFIS; Memory window; Leakage current; Band-diagram

Applied Surface Science
Room: 316 - Session AS+BI+MC+SS-MoA

The Liquid Interface & Depth Profiling and Sputtering with Cluster Ion Beams
Moderator: Ian Gilmore, National Physical Laboratory, Michaeleen Pacholski, The Dow Chemical Company

2:00pm **AS+BI+MC+SS-MoA1 Quantifying the Impact of Curvature, Convection and Complexity on Dynamic Interfacial Tension of Fluid-fluid Interfaces**, ***Lynn Walker***, Carnegie Mellon University **INVITED**

The ability to control and predict the adsorption of species at fluid-fluid interfaces is a central issue in many materials processing problems. In most processing steps, this adsorption is dynamic and part of a larger transport problem that requires understanding of local fluid flow, bulk diffusion, interfacial curvature and the details of the adsorption and desorption kinetics. We have been developing tools and a protocol to allow the details of transport of surface active species to interfaces to be quantified. Several examples of the characterization of complex fluid-fluid interfaces will be discussed. The dynamics of adsorption of single and multicomponent surfactant mixtures at oil-water and air-water interfaces has been characterized using a microtensiometer. The use of microscale interfaces allows the transport processes involved in adsorption to be analyzed and both diffusion and kinetic parameters characterized. Microscale interfaces with high curvature allow the impact of curvature to be characterized on the dynamic interfacial tension (IFT) and mechanics of the interface. The scale of the device allows the bulk solution in contact with the interface to be changed rapidly. We are able to remove the bulk surfactant at different points in during the dynamics of adsorption by rinsing the interface and continuously replacing the bulk fluid with surfactant-free aqueous phase to investigate the reversibility of adsorption. For a bulky nonionic surfactant, a critical interfacial tension arises that links the transport dynamics to the onset of partial reversibility in the system. By measuring the mechanical properties of pre-rinsed and rinsed interfaces, we also find a critical interfacial tension that leads changes in the elasticity of the interfaces. The impact of changes in interfacial coverage on coalescence and competitive adsorption are characterized to demonstrate the connection between structure of complex interfaces and interfacial behavior.

2:40pm **AS+BI+MC+SS-MoA3 *In Situ* Probing of Liquid Surfaces and Interfaces by Time-of-Flight Secondary Ion Mass Spectrometry**, ***Xiao-Ying Yu***, Pacific Northwest National Laboratory

The surfaces of aqueous phases and films can have unique kinetics and thermodynamics, distinct from the bulk. However, major surface analytical techniques are mostly vacuum-based and direct applications for volatile liquid studies are difficult. We developed a vacuum compatible microfluidic interface to enable direct observation of liquid surfaces and liquid-solid interactions. The unique aspect of our approach is that 1) the detection window is an aperture of 2-3 micrometers in diameter, which allows direct imaging of the liquid surface, and 2) surface tension is used to hold the liquid within the aperture. The microfluidic reactor is composed of a silicon nitride (SiN) membrane and polydimethylsiloxane (PDMS) . Its application in time-of-flight secondary ion mass spectrometry (ToF-SIMS) as an analytical tool was evaluated using a variety of aqueous solutions and complex liquid mixtures, some of which contain nanoparticles. Most recently, we demonstrated *in situ* probing of the electrode-electrolyte solution interface (or solid-electrolyte interface, SEI) using a new electrochemical probe based on our original invention. It provides the first direct observation of the surface and diffused layer of SEI in a liquid with chemical speciation using ToF-SIMS. Moreover, we extended the microfluidic reactor for biofilm growth and mammalian cell cultures and real-time correlative characterization by more than one spectroscopy and microscopy technique. Results from our latest development will also be presented in additional to published ones, showcasing new directions and applications using this novel approach based on microfluidics and combined vacuum and ambient spectroscopy and microscopy multimodal imaging.

3:00pm **AS+BI+MC+SS-MoA4 Mass Spectrometric Characterization of Droplet Surfaces at Ambient Pressure**, ***Kaveh Jorabchi***, Georgetown University

Mass spectrometric methods provide excellent selectivity and sensitivity for chemical characterization of samples. For these methods, ionization constitutes a key step where chemical information from the sample is encoded into populations of gas-phase ions. Investigations on electrospray ionization have shown that the ionization efficiency has a positive bias with respect to surface affinity of analytes in droplets, opening a new avenue for liquid surface analysis. This ionization bias stems from higher ion production rates for surface active analytes. To this end, we have developed a new method to monitor gas-phase ion formation rates from charged nano-droplets. A pulsed nano-spray is used to emit a cloud of charged nano-droplets within an atmospheric-pressure mobility cell. The droplets are guided by a pulsed electric field through the mobility cell, undergoing desolvation and ion production prior to detection by a time-of-flight mass spectrometer. Each chemical species within the droplets creates an ion cloud. The arrival times of the ions at the mass spectrometer are recorded by varying the on-time of the pulsed electric field within the mobility cell, enabling ion cloud size measurements. We demonstrate that the ion cloud sizes are correlated with ion production rates, reflecting interfacial propensity of the analytes. These measurements are consistent with the ion evaporation mechanism from charged nano-droplets, providing a method for liquid surface analysis based on gas-phase ion formation rates.

3:40pm **AS+BI+MC+SS-MoA6 Organic Depth Profiling Alchemy: Can We Transmute Data into Meaning?**, ***Alexander Shard***, National Physical Laboratory, UK **INVITED**

Argon cluster sources suitable for depth profiling organic materials have developed rapidly and are now widely available and routinely used to analyse materials ranging from organic electronic devices to biological samples. This fantastic progress allows detailed insight into the chemistry and structure of organic materials with depth resolutions below 10 nm over many micrometres. When combined with 2D surface chemical imaging, detailed 3D reconstructions can be obtained allowing the label-free visualisation of chemical distributions which were previously impossible to obtain. However, because detailed understanding of the processes involved is still developing, it is necessary to view such data with scepticism when a quantitative answer is required. Conversely, the ability to perform nearly damage-free profiles of organic materials allows us to answer fundamental questions about surface analytical methods provided that the sample analysed has a known structure and composition.

The recurring questions in organic depth profiling and 3D imaging relate to the depth scale and the translation of a signal into a concentration, or amount of material. At NPL, we have developed reference materials which are designed to address these questions and in this talk an overview of developments in quantitative organic depth profiling will be provided. The use of XPS is shown to provide accurate compositions, as expected. However, there are some practical issues to be understood involving X-ray and electron damage and sample heating. Additionally, XPS suffers from low sensitivity, specificity and lateral resolution compared to SIMS. Whilst SIMS is fast, specific, sensitive and has high lateral resolution it suffers from the lack of an adequate means of converting data into compositions. Here, reference materials have been constructed which enable the most important effects of the sample on SIMS data to be described. These effects are outlined and include an apparent depth of origin difference for secondary ions, surface transient behaviour and the matrix effect. It is also shown how it is possible to use the matrix effect to assess the nanoscale phase separation of materials.

4:20pm **AS+BI+MC+SS-MoA8 Argon Clusters - A Novel Solution for the Depth Profiling of Metal Alloys and Inorganic Materials**, ***Jonathan Counsell***, *H.L. Brannon, S.J. Coultas, S.J. Hutton, A.J. Roberts, C.J. Blomfield*, Kratos Analytical Limited, UK

Depth profiles are routinely used to gain information regarding elemental concentration and chemical composition of complex heterogeneous materials. Ion bombardment removes successive layers, exposing bulk material. The difference in the chemical composition of the surface relative to the sub-surface or bulk is often significant to the mechanical or electrical performance of the material.

Here we will discuss the use of Argon clusters for depth profiling a range of inorganic and alloyed materials. Traditionally, depth profiling inorganic materials employed Ar^+ as the bombardment ion. Unfortunately, monatomic Ar^+ can cause significant damage to the bulk structure of the material and can preferentially remove lighter and less well bound elements leading to misleading results. Recent studies show Argon cluster ions greatly diminish the effects of preferential sputtering with simple metal oxides such as titania.[1] Here we wish to broaden this application to a wider variety of materials including precious metal/non-precious metal binary alloys for novel electrode surfaces and ternary and quaternary chalcogenides. We show that with gentler ions, where the energy per atom can be as low as 5-40 eV, it is possible to greatly reduce bulk damage and the preferential removal of weakly bound elements in complex materials.[2]

References:

[1] J. D. P. Counsell, A. J. Roberts, W. Boxford, C. Moffitt and K. Takahashi, *J. Surf. Anal.,* **20** [3], 2014, 211–215

[2] A. Etin, G. E. Shter, R. Brener, S. Baltianski and G. S. Grader., *J. Am. Ceram. Soc.,* **90** [12], 2007, 3800–3803.

4:40pm **AS+BI+MC+SS-MoA9 Low Temperature Plasma for Crater Edge Depth Profiling of Crosslinking Organic Multilayers: Comparison with C_{60} and Argon Cluster Sputter Sources**, ***Shin Muramoto***, National Institute of Standards and Technology (NIST), *D. Rading,* ION-TOF GmbH, Germany, *B. Bush, G. Gillen,* National Institute of Standards and Technology (NIST), *D.G. Castner*, University of Washington

A model organic layer system consisting of three 1 nm delta layers of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) separated by three 30 nm layers of tris(8-hydroxyquinolinato)aluminum (Alq3) was used to evaluate the effectiveness of helium low temperature plasma (LTP) etching for the preparation of crater edge surfaces for subsequent compositional depth profile analysis. The quality of the depth profile was determined by comparing the depth resolutions of the BCP delta layers obtained from the plasma-etched craters with those obtained using ToF-SIMS dual-beam depth profiling equipped with C_{60}^{2+} and argon cluster ($Ar_{1000\ to\ 2500}$) sputter sources. Using the full width at half maximum (FWHM) of each delta peak, the depth resolutions of the second and third delta layers were measured to be 6.9 nm and 6.0 nm for the plasma-etched crater, respectively, which were very close to the depth resolutions of 6.2 nm and 5.8 nm obtained from the argon cluster depth profile. In comparison, the use of a 1/e decay length to approximate the depth resolution gave results that identified the artifacts caused by ion bombardment in SIMS depth profiling. The 1/e decay length for the trailing edge of each delta were 2.0 nm and 1.8 nm for the plasma-etched crater, respectively, while the argon cluster depth profile gave decay lengths of 3.5 nm and 3.4 nm, owing to the longer tails produced by artifacts and possibly by slower sputter rate through the delta layers. For the C_{60}^{2+} depth profile, the need to rescale the axis as a result of a strong nonlinear sputter rate gave artificially improved depth resolutions, where FWHM of the delta peaks were 5.6 nm and 7.3 nm, respectively, and 1/e decay lengths were 1.7 nm and 2.3 nm, respectively. Although some artifacts such as contaminant deposition remain, low temperature plasma was shown to be a viable option for creating crater edges for compositional depth profiling without artifacts seen in ToF-SIMS depth profiling.

5:00pm **AS+BI+MC+SS-MoA10 Desorption/Ionization induced by Neutral Cluster Impact as a Versatile Tool for the Investigation of Sensitive and Complex Biosamples**, *A. Portz,* Justus Liebig University, Germany, *M. Baur,* University of Applied Sciences, Germany, *C.R. Gebhardt,* Bruker Daltonik GmbH, Germany, ***Michael Durr***, Justus Liebig University, Germany

Desorption and ionization induced by neutral clusters (DINeC) can be employed as a soft and matrix-free method for transferring surface-adsorbed biomolecules into the gas phase. Using neutral clusters with polar constituents such as SO_2, the impacting clusters do not only provide the energy necessary for desorption but also serve as a transient matrix in which the desorbing molecule is dissolved during the desorption process. As a consequence, desorption and ionization of oligopeptides and smaller proteins can proceed at comparably low energies of the impacting clusters and without any fragmentation [1]. Using a combination of DINeC and ion trap mass spectrometry, femtomol sensitivity was achieved for standard oligopeptides such as angiotensin II or bradykinin [2]; good ion-to-neutral ratio was observed [3].

In this contribution, we show that the signal of the intact molecules $(M+H)^+$ is predominant even in the case of phospho- and glycopeptides, and typical fragments were observed only in low abundance. The origin of these fragments was investigated by comparison with ESI measurements of the original solution as well as of samples which have undergone a similar treatment as for the preparation of the DINeC samples. In that way, we could show that fragmentation takes place already during sample preparation and DINeC is suitable to directly measure such changes of the samples.

Samples with a multitude of components as obtained from realistic biotechnological processes such as tryptic digest of proteins were also successfully analyzed. Peptide mass fingerprint analysis was applied for the evaluation of the respective spectra with very good sequence coverage and protein score. When compared to ESI or MALDI, a substantial number of the unique peptides which were identified with DINeC were not detected with the other methods. Notably, even in the presence of a large excess of salt in the original solution clear spectra of the intact biomolecules were detected. The results are correlated to the very properties of the DINeC process. The method was furthermore successfully applied to a variety of different classes of molecules such as lipids, dye molecules, and pesticides.

References:

[1] C. R. Gebhardt, et. al., Angew. Chem. Int. Ed. **48**, 4162 (2009).

[2] M. Baur, et al., Rapid Commun. Mass Spectrom. **28**, 290 (2014).

[3] B.-J. Lee, et al., Rapid Commun. Mass Spectrom. **27**, 1090 (2013).

5:20pm **AS+BI+MC+SS-MoA11 C_{60} and Argon Gas Cluster Ion Sputter Depth Profiling for Quantitative Inorganic Thin Film Analysis**, ***Saad Alnabulsi***, *G.L. Fisher, S.R. Bryan, J.S. Hammond, J.F. Moulder*, Physical Electronics Inc.

A successful sputter depth profile accurately identifies layer thickness and composition of materials as a function of depth within film structures. In the case of inorganic thin films, monoatomic argon ion beam depth profiling continues to be the preferred choice despite issues with preferential sputtering, material migration, and chemical reduction that may occur during the sputter process to alter the apparent profile of the analyzed material[1][2].

The introduction of C_{60} cluster ion beam and argon gas cluster ion beam (GCIB) sputtering in recent years provided the capability of successful depth profiling of polymer and organic materials while preserving the stoichiometry and chemical structure below the surface[3] [4].

Currently, there is great interest in establishing the viability of these cluster ion sources as an alternative to monoatomic argon ion beam sources for analyzing inorganic semiconductor and glass films, with anticipated improvement in the quantitative accuracy of inorganic depth profile results [5][6].

The purpose of this study is to present a comparative evaluation of quantitative XPS analysis to demonstrate the benefits and limitations of monatomic argon, C_{60}, and argon gas cluster ion beam sputtering for compositional inorganic depth profiling.

[1] R. K. Brow. *J. of Vac. Sci. Technol. A* **7**, 1673 (1989).

[2] V. Smentkowski. *Prog. in Sur. Sci.* **64**, 1 (2000).

[3] T. Nobuta, T. Ogawa. *J. of Mater. Sci.* **44**, 1800 (2009).

[4] C. M. Mahoney. *Mass Spec. Rev.* **29**, 247 (2010).

[5] Y. Yamamoto, K. Yamamoto. *Mater. Sci. Eng.* **18** (2011).

[6] D. Kobayashi, Y. Yamamoto, T. Isemura. *Sur. and Inter. Anal.* **45** 113 (2013).

Materials Characterization in the Semiconductor Industry Focus Topic
Room: 313 - Session MC+2D+AP+AS-MoA

Characterization of III-Vs (2:00-3:20 pm)/Photovoltaics, EUV masks, etc. (3:40-4:40 pm)
Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

2:00pm **MC+2D+AP+AS-MoA1 High Resolution SIMS Depth Profiling in III-V Compound Semiconductors**, ***Marinus Hopstaken***, *M.S. Schamis, Y. Sun, A. Majumdar, C.-W. Cheng, B.A. Wacaser, G. Cohen, K.K. Chan, D.K. Sadana, D.-G. Park, E. Leobandung*, IBM T.J. Watson Research Center

Recently, there has been renewed technological interest for application of InGaAs and related III-V high-mobility materials as a potential replacement for the MOSFET Si-channel [1]. Successful integration of novel materials and processes requires accurate physical characterization of in-depth chemical distribution with nm-scale resolution. We will address some of the challenges regarding SIMS depth profiling of III-V materials and propose analytical solutions for the characterization of more complex multilayer substrates, impurities therein, and Ultra-Shallow Junction (USJ) doping profiles.

Ion beam based sputtering of III-V compounds is intrinsically more complex than in conventional Si substrates. One of the major issues with depth profiling of III-V materials is their higher sensitivity to formation of ion-beam induced topography, which has a detrimental impact on depth resolution [2]. We have previously reported anomalous sputtering behavior of (In)GaAs under low energy O_2^+ sputtering, causing severe degradation of depth resolution [3].

In case of low energy Cs^+ sputtering at oblique incidence, we have achieved uniform sputtering conditions on different III-V compounds with no significant topography formation. We have demonstrated constant depth resolution in III-V multilayer structures with decay lengths as low as 2 nm/decade at low Cs^+ impact energy (down to 250 eV).

We will address some of the analytical challenges regarding the quantification of depth and concentration scales in III-V multilayer structures, grown by hetero-epitaxy. We employ explicit corrections for yield variations using appropriate standards in their respective matrices. A special case occurs for the group IV *n*-type dopants (*i.e.* Si, Ge), which are typically monitored as negative cluster ion attached to the group V element for reasons of sensitivity. We have developed a quantification scheme to determine [Si] doping profiles in hetero-epitaxial structures, composed from the negative cluster ions (e.g. $SiAs^-$, SiP^-) in the respective matrices.

In summary, this work has improved our fundamental understanding of low-energy ion beam interactions in III-V materials, which is essential for achieving sub-nm depth resolution in thin-film structures. In addition, this work has provided with an optimum window of analytical conditions for quantitative analysis of a wide variety of impurities and dopants with high sensitivity in different III-V materials.

1. Y. Sun et al., *IEDM 2013 Conf. Proc*., p. 48-51.

2. E.-H. Cirlin, J. J. Vajo, R. E. Doty, and T. C. Hasenberg, *J. Vac. Sci. Technol. A***9**, 1395 (1991).

3. M. J. P. Hopstaken et al., *J. Vac. Sci. Technol. B***28**,1287, (2012).

2:20pm **MC+2D+AP+AS-MoA2 Nitrogen Incorporation in Dilute Nitride III-V Semiconductors Measured by Resonant Nuclear Reaction Analysis and Ion Beam Channeling**, ***John Demaree**, S.P. Svensson, W.L. Sarney*, US Army Research Laboratory

The behavior of dilute nitride III-V semiconductors depends critically on the number of nitrogen atoms residing substitutionally on Group V sites, and this small nitrogen incorporation may be used to tailor the optical bandgap for detection of electromagnetic radiation in future low-cost near-infrared imaging systems. In this study, films of GaAsN and GaSbN were synthesized using molecular beam epitaxy at various temperatures and growth rates, with the assistance of a nitrogen plasma source isotopically enriched with ^{15}N. The films were examined using x-ray diffraction, secondary ion mass spectroscopy, x-ray photoelectron spectroscopy, and resonant nuclear reaction analysis (RNRA) to assess the amount of nitrogen incorporation. Furthermore, RNRA measurements were combined with ion beam channeling methods to ascertain the fraction of incorporated nitrogen atoms residing on substitutional and interstitial lattice sites. The narrow energy resonance and corresponding high depth resolution of the nuclear reaction used (the 897 keV p,gamma reaction with ^{15}N) also enabled an assessment of the substitutional incorporation of the nitrogen throughout the thickness of the 100-400 nm thick films.

2:40pm **MC+2D+AP+AS-MoA3 Determination of Growth Conditions for Highly Mismatched Alloys, Using *In Situ* Auger Electron Spectroscopy and Flux grading**, ***Stefan Svensson**, W.L. Sarney,* US Army Research Laboratory*, M. Ting, K.M. Yu,* Lawrence Berkeley National Laboratory*, L.W. Calley*, Staib Instruments, Inc.

The electronic band structures of GaN can be effectively modified by the incorporation of Sb. Because of the high electronegativity mismatch between Sb and N growth of GaNSb by molecular beam epitaxy (MBE) must be done at relatively low temperatures and under N-rich condition in order to control the bandgap of the material. The Sb-flux must also be chosen carefully in relation to the growth rate and N-overpressure to control composition and crystallinity. These growth conditions represent a vast parameter space, which is extremely time-consuming to explore in a systematic fashion.

The typical approach for attacking such a problem is to judiciously select a limited set of parameter combinations based on experience and literature data. However, if growth windows are narrow there is no guarantee for success. To more quickly cover a larger parameter range we have grown a very limited number of samples but continuously varied one parameter at a time while employing a combination of in situ and ex situ probes that can reveal critical parameter points. The most novel piece of equipment is the in situ *STAIB Auger Probe,* which allows uninterrupted chemical analysis during crystal growth. In all of the following experiments the substrate temperature was fixed at 325 °C.

In one experiment we determined the transition between Ga- and N-rich MBE growth conditions of GaN by setting a fixed N-flow that generated a steady-state background chamber pressure of $1.5x10^{-5}$ Torr, while the Ga-source was set up to generate a linear flux ramp from $9.8x10^{16}$ to $3.9x10^{18}$ at/m^2/s over two hours. During this ramp, the Auger electron signals for N (375 eV), and Ga (1050 eV) were continuously monitored. As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N- and Ga-rich conditions and could thus determine the critical Ga-flux relative to the N gas-flow.

In a second experiment the previous information was used to set Ga- and N-fluxes to slight N-rich conditions, while the Sb-valve was slowly opened. In this case both the Auger signals and the reflection high-energy electron diffraction pattern were observed to find the transition between crystalline and amorphous growth conditions. The sample was subsequently analyzed with Rutherford backscattering, which verified the varying Sb-composition. With the data from these two test samples subsequent films were grown with the desired bandgap of 2.2 eV suitable as photoelectrodes for photoelectrochemical water splitting application.

3:00pm **MC+2D+AP+AS-MoA4 Electron Channeling Contrast Imaging: Examining Dislocation Effects in III-Ns**, *J.K. Hite,* U.S. Naval Research Laboratory*, P. Gaddipati,* American Society for Engineering Education*, **Michael Mastro**, C.R. Eddy, D.J. Meyer*, U.S. Naval Research Laboratory

III-N materials continue to play a significant role in a range of technologies from rf electronics to visible and UV emitters and detectors. This is true despite a heavy population of extended defects in the active regions of these devices, which degrade the operation, potential performance, and reliability of such devices. With such high dislocation densities when grown heteroepitaxially on sapphire or SiC (10^8-10^{10} cm^{-2}), techniques to reliably, rapidly, and non-destructively determine spatially defect density are necessary to determine the effects of these defects on device performance.

The most precise characterization tool for defect density has been transmission electron microscopy, but this is a destructive technique, as are other methods such as molten KOH or photo-electrochemical etching of the surface to reveal dislocation sites. Cathodoluminescence imaging only detects dislocations which change the optical emission of the material. X-ray diffraction can be used to extrapolate dislocation density, but not identify individual defects.

Electron channeling contrast imaging (ECCI), a non-destructive technique that has been used to examine defects in metals and ceramics, has recently seen use in III-nitride semiconductors. This technique allows for direct imaging of dislocations, grain boundaries, and topological information all at once. We will present an overview of the uses of ECCI in characterizing III-N materials, culminating in recent work applying the technique to AlGaN/GaN HEMT structures. By imaging the active areas of van der Pauw structures on a single sample with varying mobility, we find a direct negative correlation between screw dislocation and electron mobility.

3:40pm **MC+2D+AP+AS-MoA6 EUV Lithography Mask Cleaning Applications of TOF SIMS Analysis**, ***Thomas Laursen**, S.W. Novak,* SUNY College of Nanoscale Science and Engineering*, A. Rastegar,* SEMATECH*, T. Nakayama*, SUNY College of Nanoscale Science and Engineering

Extreme-UV Lithography (EUVL) is the current R&D frontier for the semiconductor industry. Developing this new technology is generating new studies into a range of new materials issues. EUVL photomask is one important branch of this technology and serious issues have been identified related to the mask surfaces. Photomask performance is usually characterized in terms of EUV (λ = 13.5 nm) Reflectivity (EUVR) and absorption. But when it comes to surface degradation by radiation exposure and mask cleaning of defects, it is valuable to complement EUVR with a surface analytical technique in order to elucidate the material changes taking place. TOF SIMS has proven to be a versatile analytical technique in this regard. While it may not be the optimal technique in each and every case, it does provide high sensitivity to compositional changes and high-resolution depth profiles. Furthermore, TOF-SIMS analysis on the IonTof V-300 can be done using full-size photomasks which allow analysis at the various stages of processing.

The surface structures on the EUV mask surface consist of a stack of thin films having thicknesses ranging from 1 to 50 nm. The reflective layer contains 40 bilayers of Mo-Si consisting of 2.7 nm Mo and 4.1 nm Si—ending with a Si layer. This multilayer is usually capped with either a 2.5 nm Ru or in some cases a 2 nm TiO_2 surface film. Metallic films with high extinction coefficient with thicknesses in the range from 35 to 75 nm are deposited as an absorber layer and patterned on Ru-capped multilayer blanks.

The combination of EUVR and TOF-SIMS analysis of the Ru capped multilayer EUV masks and blanks provided detailed information on the effects of cleaning on contamination, materials degradation and oxidation. Whereas the EUVR measurements could be directly related to mask specifications, the TOF-SIMS analysis provided more detailed information on surface contamination and oxidation levels, as well as surface-film integrity.

The interactions of the various segments constituting a cleaning process have been characterized in terms of their effect on film etching and removals as well as film oxidation. In general sulfuric acid - H2O2 -based treatments caused a severe deterioration of the film structures, whereas

NH4OH - H2O2 -based treatments (SC1) caused a more manageable deterioration. Current mask cleaning processes are therefore primarily based on SC1 cleaning. Another concern for mask defectivity is progressive defects generated by sulfate and ammonium compounds. TOF-SIMS was also used to study the aggregation of these compounds during electron irradiation (simulating EUV-irradiation conditions), which was visualized by stage-scan imaging.

4:00pm **MC+2D+AP+AS-MoA7 Characterization of Ag/CuInSe$_2$ Thin-Film Photovoltaics by Photoelectron Spectroscopy**, ***Pinar Aydogan***, Bilkent University, Turkey, *N. Johnson, A. Rockett,* University of Illinois at Urbana-Champaign, *S. Suzer*, Bilkent University, Turkey

Photovoltaic power source technology is one of the most desirable ways to provide energy for the world of tomorrow. Hence, it is important to understand the surface, electrical and photo-induced properties of these materials in order to enhance their efficiencies. Currently used materials in photovoltaic manufacturing technology are mainly crystalline silicon, CdTe (cadmium telluride), amorphous and nanocrystalline silicon, CIS (copper indium diselenide) and CIGS (copper indium gallium selenide). In this study, we focused only on the silver/copper indium diselenide cells, which contain a CdS layer on top. X-ray photoelectron spectroscopy (XPS) that we used for analysis was modified to apply both an external photo illumination and voltage bias during data acquisition. The first part of the research focuses on the result of photo induced variations in binding energies of elements and the main objective is to understand the different binding energy shifts of each element in the Ag/CuInSe$_2$ films in both wavelength- and intensity-sensitive fashion under illumination with three different continuous wave lasers. Furthermore, electrical charging properties of CIS/CdS thin film are studied with externally applied electrical square-wave pulses (SQW), so-called Dynamic XPS. Results will be presented with an ultimate aim of better understanding of the roles of defects affecting the performance of CIS devices. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).

4:40pm **MC+2D+AP+AS-MoA9 Facile Synthesis of Composition Tuned Cu$_{1-x}$Zn$_x$O Nanoarchitecture on Alpha-Brass**, *Y. Myung,* ***Sriya Banerjee***, Washington University, St. Louis, *H. Im, J. Park,* Korea University, *S. Raman,* Physical Electronics Inc., *P. Banerjee*, Washington University, St. Louis

Composition controlled Cu$_{1-x}$Zn$_x$O layers have been synthesized on pretreated a-brass followed by ambient oxidation. The pretreatment consists of a vacuum anneal step which effectively depletes the surface of Zn. The depleted Zn specimens were then oxidized at various temperatures ranging from 300°C – 600°C. SEM and XRD result shows the oxide consists of CuO/ZnO film/nanowire composite architecture. The analysis of electronic structure (XPS) and optical properties (PL) shows the formation of Zn containing alloy in the surface region of CuO films. The composition ratio of Cu and Zn were calculated based on XPS survey spectra. In particular, XPS fine spectra revealed that as the oxidation temperature increases, the binding energy of Zn 2$p_{3/2}$shifts to higher energy, suggesting the possibility of hybridization between the Zn ions and Cu ions.

Photoelectrochemical properties of Cu$_{1-x}$Zn$_x$O cathodes exhibit robust photocurrent densities (~3 mA/cm^2). We suggest the dezincification followed by thermal oxidation provides a better approach for composition tuned nanostructure design and fabrication. These semiconductor nanoarchitectures are excellent candidate materials for fabricating solar energy harvesting photoelectrodes as well as optoelectronic devices.

5:00pm **MC+2D+AP+AS-MoA10 In-line Dimensional Measurement via Simultaneous Small Spot XPS and XRF for Cu CMP Process Control**, *B. Lherron,* ST Microelectronics, ***Wei Ti Lee***, Revera, *Motoyama, Chao, Deprospo, Kim*, IBM

As Cu lines used for CMOS devices interconnections become thinner and smaller, current metrology solutions reach their limits. XRay Photoelectron Spectroscopy (XPS) and XRay Fluorescence (XRF) are commonly used as Semiconductor manufacturing process control techniques to measure composition and/or film thickness. In this paper we are exploring the use of a combination of XPS and XRF collected simultaneously to measure the dimensions (line top CD, area and thickness) of Cu lines post Cu CMP on patterned structures. A set of structures with different Cu line width and pitch were used to demonstrate the capability of XPS/XRF on this new application. Results obtained showed good correlation with predicted CD measured by XPS and line section measured by XRF .The paper will also present the comparison with cross section as well as the performance in precision, sensitivity and accuracy of the newly developed technique.

This work was performed by the Research and Development Alliance Teams at various IBM Research and Development Facilities

5:20pm **MC+2D+AP+AS-MoA11 Imaging of the Native Inversion Layer on Silicon-on-Insulator via Scanning Surface Photovoltage; Implications for RF harmonic generation**, ***Daminda Dahanayaka***, IBM, *A. Wong,* Dartmouth College, *P. Kaszuba, L. Moszkowicz, R. Wells, F. Alwine,* IBM, *L.A. Bumm,* University of Oklahoma, *R. Phelps, J. Slinkman*, IBM

Imaging of the native inversion layer on Silicon-on-Insulator via Scanning Surface Photovoltage;

Implications for RF harmonic generation

Daminda Dahanayaka[1], Andrew Wong[2], Phil Kaszuba[1], Leon Moszkowicz[1], Randall Wells[1], Frank Alwine[1], Lloyd A. Bumm[3], Richard Phelps[1] and James Slinkman[1]

[1]IBM Microelectronics, 1000 River Street, Essex Junction, Vermont 05452

[2]Thayer School of Engineering, Dartmouth College, 14 Engineering Drive, Hanover, NH 03755

[3]Homer L DodgeDepartment of Physics and Astronomy, University of Oklahoma, 440 W. Brooks Street, Norman, OK 73019

Email: damindahd@us.ibm.com

One of the major challenges encountered during the development of IBM's state-of-the-art RF CMOS Technology on Silicon-on-Insulator (SOI) was to overcome the adverse effects on the harmonic performance of stacked switch devices and transmission lines due to the presence of trapped positive charge, Q^+, at the interface of the buried oxide (BOX) and the underlying high-resistivity substrate (SX). Most commercially available standard SOI substrates for RF applications have specifications to maintain Q^+ less than 10^{11} cm^{-2}. The substrate resistivity for IBMs technology is specified to be greater than 1000 ohm-cm, (p-type), i.e. $p_0 \approx 5 \times 10^{13}$ cm^{-3}. This combination induces a "built-in" n-type inversion layer just under the BOX/SX interface. Using "Scanning Surface Photovoltage" (SSPV) microscopy, we present the first data to show quantitatively the extent of this inversion layer into the substrate. The technique disclosed here quantifies the inversion layer, the degree to which it can be suppressed, and has led to further enhancements to the RF technology on SOI, such as substantial NFET off-state leakage reduction.

References

[1] A. Botula et al., IEEE Topical Meeting on Silicon Monolithic Integrated Circuits in RF Systems, 2009. SiRF '09, 1-4 (2009).

[2] L.A. Bumm et al., US Patent No. 7,944,550.

[3] T. Ohno,IEDMTech. Digest, 627-630 (1995).

[4] J. Greco et al., US Patent No. 8299537 B2.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-TuM

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)
Moderator: Franklin (Feng) Tao, University of Notre Dame

8:00am **IS+AS+MC+SS-TuM1 The ISISS Facility at BESSY II and Beyond: The Application of Near Ambient Pressure X-ray Electron Spectroscopy in the Surface Characterization of Technical Catalysts**, ***Michael Hävecker***, Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *Ch. Heine, M. Eichelbaum,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, *F. Rosowski,* BasCat, UniCat-BASF JointLab, Germany, *A. Trunschke, R. Schlögl*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

The surface of functional materials like catalysts responds to the ambient conditions. Surface sensitive in-situ spectroscopy, i.e. in the presence of a reactive gas allows studying the formation of the gas/solid interface of a catalyst. The ISISS facility operated by the FHI at the synchrotron radiation source BESSY II of the HZB is dedicated to this kind of in situ studies [1 - 3]. Online gas analytics allows correlating the electronic surface structure with the catalytic performance. Examples for the dynamic formation of the electronic surface structure by interaction with the ambient gas under equilibrium will be presented focusing on technical catalysts like multi-element mixed oxide powders. The direct catalytic oxidation of alkanes to olefins and oxygenates is becoming increasingly important for the chemical industry due to the up-coming shortage of crude oil resources. Vanadyl pyrophosphate is the industrially used catalyst in the selective oxidation of n-butane to maleic anhydride. We characterized the surface of this catalyst material with NAP-XPS in the mbar pressure range and with NAP-soft XAS in the electron yield mode at pressures up to 1000mbar at various gas mixtures. In addition to the determination of composition and vanadium oxidation state also semiconductor properties like work function changes and Fermi level pinning have been studied [4].

Finally, an outlook on future activities at HZB/BESSY to develop further synchrotron based ambient pressure characterization methodologies will be given. The Energy Materials In-Situ Laboratory Berlin (EMIL) is a research alliance of the HZB and FHI that will include a NAP-high kinetic energy XPS endstation capable to operate at kinetic energy of photoelectrons up to 7000eV that allows studying buried layers and liquid/solid interfaces.

References

Salmeron, M., Schlögl, R., Ambient pressure photoelectron spectroscopy: A new tool for surface science and nanotechnology. Surf. Sci. Rep., 32, 1022 (2008).

Bluhm, H., Hävecker, M. et al., In situ x-ray photoelectron spectroscopy studies of gas-solid interfaces at near ambient conditions, MRS BULLETIN., 63, 169 (2007).

Bluhm, H. et al., Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy. Chem. Soc. Rev., 42, 5833 (2013).

Heine, Ch. et al., Work function, band bending, and microwave conductivity studies… J. Phys. Chem. C, 117, 26988 (2013).

8:40am **IS+AS+MC+SS-TuM3 Recent Trends and Instrument Development in Ambient Pressure Photoelectron Spectroscopy**, ***Henrik Bergersen***, *J. Åhlund*, VG Scienta AB, Sweden

The field of Ambient Pressure Photoelectron Spectroscopy (APPES) has gone through rapid development in recent years. Although the field was pioneered in the 1970's, most instrument as well as application development has happened in the last decade. In this contribution we will discuss some recent trends in APPES and present state-of-the-art work within the different applications areas.

Experiments done under normal surface science conditions (Ultra High Vacuum) are of limited use in some applications, e.g. catalysis, due to the pressure gap problem. This motivates the study of systems at ambient pressures. While the presence of a gas atmosphere surrounding the sample enables new types of studies, it also poses instrumentation difficulties. The most notable of these is signal decrease due to inelastic scattering of the photoelectrons in the surrounding gas. We will show state-of-the-art solutions to limit this scattering together with recent results.

Photoelectron spectroscopy went through a revolution in the 1990's, with the development of parallel angular detection using 2D detectors, a development that VG Scienta is proud to have contributed to. The possibility of simultaneous recording of Angular Resolved PES (ARPES) spectra enables not only band structure measurements, but also x-ray photoelectron diffraction (XPD), depth profiling and standing wave spectroscopy. Recent examples within APPES will be given.

The use of 2D detectors to record parallel spatially resolved spectra is a related technique. Here we will show experimental results as well as very recent instrument development to obtain world leading spatial resolution at ambient conditions.

The combination of APPES and Hard X-ray Photoelectron Spectroscopy (HAXPES) has recently become an established technique. We will show results of the use of this combination to decrease inelastic scattering of the photoelectrons as well as to tailor the probing depth of advanced systems.

In APPES, more than in UHV PES, instrument usability and sample handling is a key to successful measurements. VG Scienta has developed several complete system offerings to maximize productivity in the lab. These will be discussed on a conceptual level, as well as in some detail.

9:00am **IS+AS+MC+SS-TuM4 *In Situ* Studies of Exceptionally Active Catalyst of Earth Abundant Elements for Complete Combustion of Methane at a Relatively Low Temperature**, *F. Tao, J. Shan, L.T. Nguyen, S. Zhang,* ***Weixin Huang***, University of Notre Dame

It is critical to develop a catalyst made of earth-abundant elements highly active for a complete combustion of CH_4 at a relatively low temperature for catalytically transforming CH_4 to electrical energy in power plant. The currently available catalysts with high activity consist of precious metal nanoparticles supported on rare earth oxides. Their high cost limits the application of these catalysts at industrial scale. Here we report a new catalyst, early transition metal oxide-based mixed oxide only consisting of earth-abundant elements which can completely combust CH_4 at 350°C at a gas hourly space velocity of 240,000 ml 0.5% CH_4 on 1 gram in one hour. This comparable or even higher catalytic activity results from the integration of Ni cations and surface lattice oxygen atoms at the atomic scale. With such an integration, the carbon atom dissociated from CH_4 can bond with its neighboring surface oxygen atoms to form an intermediate of CO_2 and then desorb.

In-situ studies of catalyst surface using AP-XPS and monitoring of products formed from isotope-labeled catalysts show that (1) molecules O_2 dissociates on surface oxygen vacancies, (2) half of the dissociated oxygen atoms stay in oxygen vacancies, (3) the other half of dissociated oxygen atoms directly bond with hydrogen atoms dissociated from CH_4 to from OH and then H_2O molecules, (4) CH_4 progressively dissociates on Ni cations to form CH_n (n=3, 2, 1, 0), (5) carbon atoms bind to two surface lattice oxygen atoms nearby to form a carboxylate species, O-C-O intermediate, and then desorb. The mixed cations and surface lattice oxygen atoms in this mixed oxide at atomic level makes the formation of an –O-C-O- intermediate at a mild temperature since a spillover of dissociated species is not necessary.

9:20am **IS+AS+MC+SS-TuM5 Ambient Pressure XPS Studies of Fuel Cell and Electrolysis Catalysis**, ***Hirohito Ogasawara***, SLAC National Accelerator Laboratory **INVITED**

Fuel cell and electrochemical reactions were studied by ambient pressure X-ray photoemission spectroscopy at Stanford Synchrotron Radiation Lightsource (SSRL) [1]. We will present our recent studies: platinum catalyst under different operating conditions of oxygen reduction fuel cell reaction, iridium oxide catalyst during the oxygen evolution reaction and molybdenum sulfides catalyst during the hydrogen evolution reaction. Surface changes under these electrochemical reactions, which are keys to understanding activity and durability will be shown [2,3].

[1] Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry, CatalysisToday 205 (2013) 101.

[2] Direct observation of the oxygenated species during oxygen reduction on a platinum fuel cell cathode, Nature Communications 4 (2014) 2817

[3] In situ observation of surface species on iridium oxide nanoparticles during the oxygen evolution reaction, submitted

11:00am **IS+AS+MC+SS-TuM10 Environmental Cells with 2D Electron Transparent Windows for Ambient Pressure Photoelectron Imaging and Spectroscopy**, ***Andrei Kolmakov***, National Institute of Standards and Technology (NIST)

We have designed and characterized electron transparent windows for environmental cells dedicated for ambient pressure XPS spectroscopy and electron microscopy of liquid and gaseous samples. These windows made of single or multi-layered graphene have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons what allow to conduct

interfacial spectroscopy of fully hydrated samples without differential pumping setup. In addition, these membranes are thermally and chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in graphene fabrication and transfer protocols we demonstrate the capability to perform in situ XPS and electron microscopy studies of the electrochemical processes taking place at liquid electrolyte-solid interface.

11:20am **IS+AS+MC+SS-TuM11 The Effect of Interfacial Ethanol on Ionic Distributions in Aqueous Solution**, ***Marijke Van Spyk**, K.A. Perrine, M.J. Makowski,* University of California Irvine*, H. Bluhm,* Lawrence Berkeley National Laboratory*, J.C. Hemminger*, University of California Irvine

In this study, liquid microjet X-ray photoelectron spectroscopy (LJ-XPS), carried out at beam line 11.0.2 of the ALS synchrotron at LBNL, was used to probe the interfacial behavior of aqueous magnesium or sodium chloride solutions with the addition of organics including ethanol under one torr of water vapor. Our results address fundamental issues of solvation at the surface and in the bulk of ternary solutions. For these studies, aqueous ethanol solutions were generated, and salt was added to produce an ionic solution. The ternary solution is pumped continuously through a temperature-controlled quartz capillary to produce a micron-sized laminar jet within 0.5 mm of the PES analyzer aperture. Synchrotron radiation ionizes the solution, and ejected photoelectrons are detected using differentially pumped electron optics. Tunable photon energy, together with the inelastic scattering attenuation of photoelectrons in solution, provide a variable probe depth. Here, photoelectrons with low kinetic energies (200 eV) are detected from the surface of solution, and those with high kinetic energies (600 eV) are detected from deeper into solution, where chemistry is consistent with bulk solution. The high kinetic energy photoelectrons have sufficiently large inelastic mean free paths so that a percentage are not attenuated by inelastic scattering.

Carbon (C1s), oxygen (O1s), sodium (Na2s), magnesium (Mg2s), and chloride (Cl2p) photoelectron spectra were collected at two photoelectron kinetic energies to investigate the relative concentration of species at the surface and in the bulk for various ethanol concentrations. The C1s spectra were deconvolved into two gas phase and two solution phase peaks corresponding to the carbon groups in ethanol. Surface adsorption was evident for aqueous ethanol without ions, and was diminished in the presence of ions. The relative ionic propensities at the surface change with ethanol concentration. In particular, the solvation of magnesium was impacted by dehydration. Understanding the interfacial solute distribution of these ternary solutions is important for predicting reactivity at aqueous surfaces.

11:40am **IS+AS+MC+SS-TuM12 Studying Zeolites and Clays with the Tools of Surface Science from UHV to Near-Ambient Pressures**, ***Jorge Boscoboinik***, Brookhaven National Laboratory **INVITED**

While Surface Science provided useful insights into a variety of materials of interest for catalysis, its contribution to the understanding of zeolites and clays has been limited. This was mainly due to the lack of suitable well-defined surfaces that successfully mimic the properties of these important materials while allowing its analysis using the vast toolkit of surface science. This talk will describe an aluminosilicate ultra-thin (~ 0.5 nm) film that was recently synthesized, which provides a good model system for zeolites and clays. It consists of a bilayer structure, as shown in the figure, and it counts with bridging hydroxyl groups. The latter are the active sites in zeolite catalysts, of great importance for energy transformations such as the cracking of crude oil and the methanol to gasoline conversion. This model system allows then to study the interaction of molecules involved in these catalytic processes and potentially contribute to the understanding of these chemical transformations. I will provide first a description of the system itself as characterized in ultra-high vacuum (UHV) conditions and then move on to analyze the interaction of these aluminosilicate films with different molecules of interest from UHV to near-ambient pressures.

References

[1] J.A. Boscoboinik, X. Yu, B. Yang, F.D. Fischer, R. Wlodarczyk, M. Sierka, S. Shaikhutdinov, J. Sauer, H.-J. Freund, Angew. Chem. Int. Ed. 51 (2012) 24, 6005-6008. Angew. Chem. 124 (2012) 6107-6111.

[2] J.A. Boscoboinik, X. Yu, B. Yang, S. Shaikhutdinov, H.-J. Freund. Micropor. Mesopor. Mater. (2013) 165, 158-162.

[3] J.A. Boscoboinik, X. Yu, E. Emmez, B. Yang, S. Shaikhutdinov, F. Fischer, J. Sauer, H.-J. Freund. J. Phys. Chem. C (2013) 117, 13547-13556.

2D Materials Focus Topic
Room: 310 - Session 2D+AS+HI+MC+NS+PS+SP+SS-TuA

2D Materials Characterization including Microscopy and Spectroscopy
Moderator: Manish Chhowalla, Rutgers University

2:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA1 Layer-Dependent Electronic and Physical Structure of 2D van der Waals Crystals**, ***Richard Osgood***, Columbia University **INVITED**

Because of their weak Van der Waals interlayer bonding transition-metal dichalcogenide (TMDC) semiconductors can be fabricated into atomically thin two-dimensional (2D) crystals with substantial ~ 1-2 eV bandgaps. As one example, monolayer MoS_2 consists of a single layer of Mo atoms sandwiched between two layers of S atoms in a trigonal prismatic structure. The TMDC 2D system has attracted great interest because of its distinctive electronic and optical properties, such as (i) a transition from indirect-to-direct band gap in going from the multilayer to monolayer crystal due to a missing interlayer interaction in monolayer form and (ii) strong spin-orbit-coupling-induced split valence bands, i.e. 100's of meV, due to broken inversion symmetry, which makes TMDCs interesting for spin-physics physics and devices. Both properties have been predicted with density functional theory (DFT) calculations and indirectly demonstrated using photoluminescence and Raman spectroscopy.

Recently we have made a series of direct observations of the thickness-dependent electronic-band and crystal structure of TMDCs of both exfoliated and CVD grown sample. Because of the relatively modest sample sizes we have used micrometer-scale, angle-resolved photo-emission spectroscopy (micro-ARPES) of both the exfoliated and chemical-vapor-deposition-grown crystals; these measurements provide direct evidence for the shifting of the valence band maximum from gamma bar (Brillouin zone center) to kappa bar (Brillouin zone corner), as the sample thickness decreases from bulk to monolayer. Our initial results were with MoS_2 and are described in a preliminary way in Refs 1 and 2. Our TMDC experimental results are compared with rigorous DFT calculations of both the bands and the UV transitions matrix elements. The results show an evolution in band structure, which is consistent with an indirect-to-direct bandgap transition in going from few-layer to monolayer TMDC and can be attributed to changes in quantum confinement as the number of layer decreases. Our microARPES and, subsequently, higher resolution nanospectroscopy data provide clear measurements of the hole effective mass, the strain present in the monolayer crystal films, and the valence-band spin-orbit splitting. Our results explain the low hole mobility of monolayer MoS_2 compared to thicker MoS_2 and show clearly the strong orbit split energies. Our results, using nanoLEED and LEEM also provide insight into the structure and defects in monolayer films. Experiments using K-doping of single-crystal samples and resulting level shifts are also described.

1. W. Jin, P.-C. Yeh, N. Zaki, D. Zhang, J. T. Sadowski, A. Al-Mahboob, A. M. van der Zande, D.l A. Chenet, J. I. Dadap, I. P. Herman, P. Sutter, J. Hone, R. M. Osgood, Jr., "Direct Measurement of the Thickness-Dependent Electronic Band Structure of MoS_2 Using Angle-Resolved Photoemission Spectroscopy." Phys. Rev. Lett. **111**, 106801 (2013)

2. Po-Chun Yeh, Wencan Jin, Nader Zaki, Datong Zhang, Jerzy T. Sadowski, Abdullah Al-Mahboob, Arend M. van der Zande, Daniel A. Chenet, Jerry I. Dadap, Irving P. Herman, Peter Sutter, James Hone, and Richard M. Osgood, Jr., "Probing substrate-dependent long-range surface structure of single-layer and multilayer MoS_2 by low-energy electron microscopy and microprobe diffraction," Phys. Rev. B **89**, 155408 (2014)

3:00pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA3 X-ray Photoemission and Electron Energy Loss Spectroscopy Investigation of the Band Gap and Band Alignment for h-BN and MoS_2 Materials and Interfaces**, ***Benjamin French***, *J. Brockman, M. French, M. Kuhn, J.D. Bielefeld, S.W. King,* Intel Corporation*, E. Bersch, G. Bersuker,* SEMATECH*, J. DiStefano, Y.C. Lin, J.A. Robinson*, Penn State University

Hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS_2) are two dimensional (2D) materials of significant interest for future nano-electronic devices. Due to a wide band gap (~ 6 eV), close lattice matching (< 2%) and atomic planarity, hexagonal boron nitride (h-BN) is of primary interest as a potential substrate and gate dielectric in graphene channel transistor devices. In contrast, MoS_2 is a 2D semiconducting material with a band gap of ~ 1.8 eV that is attractive as a possible complement or alternative to graphene for nano-electronic devices requiring a large band gap. A key property for the success of both h-BN and MoS_2 in such devices is the interfacial band alignment with graphene, the gate contact metallization and the surrounding insulating dielectric materials. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the Schottky barrier and valence band offsets present at the interfaces between plasma enhanced chemically vapor deposited amorphous h-BN:H and chemically vapor deposited MoS_2. In combination, we have utilized reflection electron energy loss spectroscopy (REELS) to investigate the band gap of both h-BN and MoS_2 materials to deduce the conduction band alignment. We show that in many instances the valence and conduction band offsets are significant and favorable for MoS_2/h-BN transistor devices.

3:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA4 STM/STS Characterization of MoS_2 Monolayers and Nanostructures**, *A. Mills, C. Chen,* Virginia Tech*, Y. Yu, L. Cao,* North Carolina State University*,* ***Chenggang Tao***, Virginia Tech

Atomically thin molybdenum disulfide (MoS_2) and nanostructures have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. Especially, monolayer MoS_2, an atomically thin semiconductor with a direct band gap, as opposed to an indirect band gap in bulk MoS_2, has been demonstrated as field effect transistors, optoelectronic devices and chemical sensors. In our experimental study, Monolayer MoS_2 and MoS_2 triangular nanostructures are synthesized through a self-limiting chemical vapor deposition (CVD) approach. The precursor materials, $MoCl_5$ and sulfur, react at high temperatures to produce MoS_2 species and subsequently precipitate onto substrates to yield MoS_2 films and triangular nanostructures. Using scanning tunneling microscopy (STM), we have investigated the structural and electronic properties of monolayer MoS_2 grown on glassy carbon and triangular MoS_2 nanostructures on highly ordered pyrolytic graphite (HOPG). We will also discuss our scanning tunneling spectroscopy (STS) measurements on these structures.

4:40pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA8 Surface Characterization of Metal Oxide Layers Grown on CVD Graphene and Spin Precession Measurements**, ***Akitomo Matsubayashi***, University at Albany-SUNY, *W. Nolting,* University of Albany-SUNY*, D. Sinha,* University at Albany-SUNY*, A. Jayanthinarasimham, J.U. Lee,* University of Albany-SUNY, *V.P. LaBella*, University at Albany-SUNY

Ultra thin metal oxide films grown on graphene can be utilized as dielectric barriers between metals and graphene to help isolate a metal contact from the graphene channel for device applications. This is particularly important for graphene based spintronic devices as tunnel barriers between the ferromagnetic metal as a spin injector and graphene have been known to increase the spin relaxation time measured utilizing non-local detection technique of spin precession by avoiding the conductivity mismatch problem. However, simply depositing metal oxide layers such as aluminum oxide on graphene results in non-uniform film lowering the quality of the interface barrier. We will present a systematic study of aluminum oxide layers grown on CVD graphene under ultra-high vacuum conditions with and without titanium seed layers. The aluminum oxide layers with the 0.2 nm titanium seed layers showed reduced surface roughness. The chemical and structural composition determined by XPS will be also presented that shows full oxidation of the aluminum and partial oxidation of the titanium. The I-V characteristic study performed to electrically evaluate the metal oxide and the preliminary results of non-local spin precession measurements will be also addressed.

5:00pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA9 Morphology of CVD-grown Hexagonal Boron Nitride on Cu Foils**, ***Karthik Sridhara***, *W.G. Cullen,* University of Maryland, College Park*, J.K. Hite,* Naval Research Laboratory*, M.S. Fuhrer,* Monash University, Australia*, D.K. Gaskill, B.N. Feigelson*, Naval Research Laboratory

Hexagonal boron nitride (h-BN) has grown into prominence as a dielectric for graphene heterostructures. h-BN and graphene have been grown using chemical vapor deposition on various transition metal substrates. Compared to graphene, the morphology of CVD-grown h-BN on Cu has not been as widely studied. Here, we present a systematic study of the morphology of hexagonal boron nitride (h-BN) grown on polycrystalline Cu foils by chemical vapor deposition. The growth of h-BN is performed at ~1000°C in atmospheric pressure CVD with Ammonia Borane (H3NBH3) as the precursor. The copper foils, used as catalytic substrates, are thermally annealed at ~1030°C for >5 hours prior to growth and cooled slowly following growth termination. We utilized Ultra-high vacuum Scanning Tunneling Microscopy (STM), ambient AFM and SEM to assess the morphology of the CVD grown h-BN films. Highly symmetric single

crystallites of h-BN are observed for sub-monolayer growth, in agreement with recent reports. We consistently observe a corrugated topographic structure within the h-BN crystallites which is distinctly different from the surrounding copper surface, and this is consistently seen in STM, AFM, and high-resolution SEM. Our aim is to understand the nature of this difference and whether it might be due to effects of differential thermal contraction between h-BN and copper. However, complications arise due to possible changes in the copper substrate topography post-growth due to surface oxidation of the copper. Preliminary results with lateral force microscopy (LFM, frictional mode) show that these corrugations are unidirectional in a single Cu grain irrespective of the orientation of the h-BN crystal and generate frictional forces 200% greater than on the surrounding copper surface, reminiscent of earlier reports of unique frictional behavior in atomically-thin membranes [1]. STM and AFM are also used to study the twin crystal boundaries of h-BN. Preliminary STM observations indicate that merging h-BN crystals consistently have a gap of about 5 nm between them. The results of this study are independent of small variations of growth conditions.

References:

[1] C. Lee, Q. Li, W. Kalb, X.-Z. Liu, H. Berger, R. Carpick, and J. Hone, "Frictional characteristics of atomically thin sheets," Science (New York, N.Y.), vol. 328, no. 5974. pp. 76–80, 01-Apr-2010.

5:20pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA10 Influence of Chemisorbed Oxygen on the Growth of Graphene on Cu(100) and Cu(111) by Chemical Vapor Deposition**, ***EngWen Ong***, University at Albany-SUNY, *Z.R. Robinson*, U.S. Naval Research Laboratory, *T.R. Mowll, P. Tyagi*, University at Albany-SUNY, *H. Geisler*, SUNY College at Oneonta, *C.A. Ventrice, Jr.*, University at Albany-SUNY

The influence of chemisorbed oxygen on the growth of graphene by catalytic decomposition of ethylene in an ultra-high vacuum (UHV) chamber on both the Cu(100) and Cu(111) surfaces has been studied. A custom UHV compatible heater stage was constructed that allows heating of a crystal to temperatures as high as 1000 °C at hydrocarbon pressures of up to 100 mTorr. System recovery to the low 10^{-10} Torr range is achieved within a few minutes of opening the gate valve to the turbo pump. The crystal structure of the graphene films was characterized with in-situ low energy electron diffraction (LEED), and the growth morphology was monitored by ex-situ scanning electron microscopy (SEM). For the clean Cu(100) substrate, heating from room temperature to the growth temperature while dosing with ethylene resulted in the formation of epitaxial graphene films. The crystal quality was found to depend strongly on the growth temperature. At 900 °C, well-ordered two-domain graphene films were formed. For the Cu(111) surface, heating from room temperature to the growth temperature while dosing with ethylene did not result in the formation of graphene. This is attributed to the lower catalytic activity of the (111) surface and the relatively high vapor pressure of the Cu surface. The use of an Ar overpressure to suppress Cu sublimation during the growth resulted in the formation of predominately single-domain epitaxial graphene films. Predosing either the Cu(100) or Cu(111) surface with a chemisorbed layer of oxygen before graphene growth was found to adversely affect the crystal quality of the graphene overlayers by inducing a much higher degree of rotational disorder of the graphene grains with respect to the substrate. The SEM analysis revealed that the nucleation rate of the graphene islands dropped by an order of magnitude after predosing either the Cu(100) or Cu(111) surface with a chemisorbed oxygen layer before growth. On the other hand, the average area of each graphene island was observed to increase by at least an order of magnitude. Therefore, the presence of oxygen during graphene growth affects both the relative orientation and average size of grains within the films grown on both substrates.

5:40pm **2D+AS+HI+MC+NS+PS+SP+SS-TuA11 Novel Materials Properties at Atomically Thin Limit**, ***Zhi-Xun Shen***, Stanford University **INVITED**

In this talk, I will discuss recent progresses in uncovering novel materials properties at ultra-thin limit, with focus on mono-unit-cell superconductor FeSe and semiconductor MoSe2 respectively.

The observation of a large superconducting-like energy gap which opens at temperatures up to 65 K in single unit cell (1UC) thick iron selenide films on SrTiO3(FeSe/STO) has generated tremendous interest. A challenge is to understand the cause of enhanced Cooper pairing strength in this system, and possibly increase superconducting Tc. In this talk, we show angle-resolved photoemission spectroscopy, mutual inductance, and other measurements on 1UC and multi-UC thick FeSe films grown on Nb-doped SrTiO3. Our data provide clear evidence for strong cross-interface electron-phonon coupling in single UC, raising the possibility that large pairing gap are caused by the strong coupling between the FeSe electrons and certain collective modes of SrTiO3. This suggests a pathway of "integrated functional components" approach to boost superconducting properties.

The intense interest of quantum systems in confined geometries is further amplified by the recent discovery of large enhancement in photo-luminescence quantum efficiency and a potential route to "valleytronics" in atomically thin layered transition metal dichalcogenides (TMDs) MX2 (M = Mo, W; X = S, Se, Te), which are closely related to the indirect to direct band gap transition in the single layer limit. Using angle-resolved photoemission spectroscopy (ARPES) on high quality thin film samples of MoSe2 grown by molecular beam epitaxy (MBE), we have made a direct observation of a distinct transition from indirect to direct band gap as the thickness of the sample is reduced to a monolayer. The experimental band structure indicates a stronger tendency of monolayer MoSe2 towards direct band gap with larger gap size than theoretical prediction. A comparison of directly measured ARPES band gap and optical data led to important new insights on semiconductor physics in 2D. Moreover, our finding of a significant spin-splitting of ~180meV at the valence band maximum (VBM) of a monolayer MoSe2 film could greatly expand its possible application in spintronic devices.

If time permits, I will also discuss the superconductivity in CaC6 and its implication on a possible pathway for superconducting graphene.

Applied Surface Science
Room: 316 - Session AS+MC+SS-TuA

Analysis of Modified Surfaces
Moderator: Xia Dong, Eli Lilly and Company, Carl Ventrice, Jr., University at Albany-SUNY

2:20pm **AS+MC+SS-TuA1 Analysis of Surface-oxidized Polypropylene Films**, ***Mark Strobel***, *S.J. Pachuta, D. Poirier, H. Lechuga*, 3M Company **INVITED**

The most widely used industrial processes for modifying the surfaces of polymer films are flame and corona (dielectric barrier discharge) treatments. While both of these processes oxidize a thin surface region of the treated films, there are significant differences between the surfaces generated by the two surface-oxidation processes. A principal difference between corona and flame treatments is the likelihood to form water-soluble low-molecular-weight oxidized material (LMWOM). LMWOM is formed by the simultaneous oxidation and chain scission of a polymer material. LMWOM is an important surface characteristic that has a large effect on the wetting and adhesion properties of polymer surfaces.

LMWOM can be investigated by a number of surface analytical techniques, including x-ray photoelectron spectroscopy (XPS or ESCA), static secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), and contact angle measurements. This presentation will demonstrate how surface analysis enables the detection and detailed characterization of the LMWOM formed by the flame and corona treatment of polypropylene (PP) film surfaces. The mechanism of LMWOM formation can be then determined from these analytical results when coupled with an understanding of the bulk photo-and-thermal degradation of PP materials.

3:00pm **AS+MC+SS-TuA3 XPS Analysis for Modified Fabrics**, ***Christopher Deeks***, Thermo Fisher Scientific, UK, *M. Milošević, M. Radoičić, Z. Šaponjić*, University of Belgrade, Serbia, *T.S. Nunney*, Thermo Fisher Scientific, UK, *M. Radetić*, University of Belgrade, Serbia

Modifications of fabrics are becoming more important for a wide variety of applications. For example, loading TiO_2 onto cotton can improve many of the material properties, such as anti-bacterial effects, UV protection, and stain resistance.

The conformity of these modifications across sample surfaces are an important part of the application process. By using XPS in addition to other techniques, surface concentration and conformity can be determined and deduced whether the samples have met certain criteria, and how the uniformity, of lack thereof, can affect the desired outcome of the modifications.

This presentation will look at the possibility of in situ photoreduction of Ag ions on the surface of TiO_2 nanoparticles to create "active fabrics", and will utilise XPS imaging to determine whether deposition on the surface of different fabrics has been successful.

3:20pm **AS+MC+SS-TuA4 Characterization of Corona Treated Polymers**, ***Michaeleen Pacholski***, The Dow Chemical Company

Corona treatment is often used to increase the surface energy and surface polarity of polyolefins and other polymers. In this study corona-treated,

formulated polyolefin was characterized over the course of one year by SIMS, XPS and surface energy. The changes in surface chemistry could be fit to simple models to predict long-term behavior. This system is more complex than many others discussed in literature, as the formulation ingredients change in surface concentration with time, in addition to the typical decrease in surface oxygen concentration over time. SIMS and XPS measurements were used to characterize the complex surface changes as the surface energy was monitored. Additional examples of corona treated PET will also be presented.

4:20pm **AS+MC+SS-TuA7 Investigation of Atmospheric Pressure Plasma Jet as a Pre-Treatment for Adhesive Bonding of Structures Made of Carbon Fiber Reinforced Plastics (CFRP)**, ***Timo Hofmann***, *J. Holtmannspötter,* Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany*, T. Meer,* Airbus Group Innovations, Germany*, J. Rehbein, G. Härtl*, Bundeswehr Research Institute for Material, Fuels and Lubricants, Germany

Carbon fiber reinforced plastics (CFRPs) are increasingly employed in novel aircraft structures due to their high tensile strength, low weight, favorable fatigue behavior, and ruggedness against outer influences (corrosion). Joining of CFRP structures is currently performed using rivets and bolts. In order to exploit further weight-saving potential, the usage of adhesive bonding is intended.

An important key factor for the success of adhesive bonding is the surface pre-treatment of the adherents. Peel-plies are commonly used for the fabrication of CFRP structures and, in theory, are said to create a pristine and uncontaminated fractured surface upon removal. In reality, the presence of release agents leads to contaminated surfaces that may cause unforeseeable failures of structures in service.

In this contribution, CFRPs (Hexcel 8552 / IM7) were produced using various peel-plies and release foils currently employed in aerospace manufacturing processes. Atmospheric pressure plasma jet (APPJ) was investigated as a method to further improve adhesion and to clean the samples from release agents.

We present a detailed investigation of the surface morphology and composition of CFRPs before and after treatment with APPJ. The peel-plies and the CFRP surfaces were examined by a combination of Field-Emission Scanning Electron Microscopy (FE-SEM), X-Ray Photoelectron Spectroscopy (XPS), and Energy-Dispersive X-ray spectroscopy (EDX).

We studied the approach of surface functionalization and contaminant removal by variation of the type of peel ply, release agent, and plasma treatment parameters. In the experiments particular focus was placed on determining changes in the chemical composition of the surface and morphology. We demonstrate that APPJ-processes offer limited cleaning capabilities for CFRP surfaces. Furthermore, the ability to induce morphological changes is highly dependent on the initial level of surface roughness and chemistry. Finally, we show that overtreatment leads to degradation of the epoxy component and enrichment of the thermoplastic portion of the matrix on the surface.

4:40pm **AS+MC+SS-TuA8 Thickness and Composition Determination of Thin Film Sn-Oxides Growth at Room Temperature using XPS Spectra**, *M. Bravo-Sanchez,* CINVESTAV-Queretaro, Mexico*,* ***Jorge Huerta-Ruelas***, Instituto Politecnico Nacional, Mexico*, A. Herrera-Gomez*, CINVESTAV-Queretaro, Mexico

The knowledge of the tin oxidation process is important for the development corrosion-free coatings and the engineering of alloys and compounds with specific functional properties. Tin, pure and well controlled oxidized samples were characterized by X-ray photoelectron spectroscopy (XPS). All samples were prepared on Si (100) substrates with RCA treatment before Sn deposition. The thickness of the Sn layer was approximately 100 Å as measured by a thickness monitor. The pure Sn sample was measured without ambient exposure. The oxidized samples were obtained by exposing pure Sn samples to pure oxygen at a pressure of $1x10^{-4}$ Torr. Three different exposure times were used: 10, 180 and 1200 seconds. To fit XPS spectra, traditional and novel method (using a double-Lorentzian) were employed to calculate thickness and composition of the oxide layer. High resolution transmission electron microscopy measurements were performed to validate calculations. Structural parameters obtained with different XPS data fitting approaches were compared, showing a clear advantage of the double-Lorentzian method in the understanding of the initial stages of tin oxidation.

5:00pm **AS+MC+SS-TuA9 Understanding the Physiochemical and Ice-Nucleation Properties of Bare and Sulfuric Acid Coated Atmospheric Mineral Dust Aerosols**, ***Manjula Nandasiri***, *N. Madaan, A. Devaraj, G.R. Kulkarni, T. Varga, V. Shutthanandan, S.A. Thevuthasan*, Pacific Northwest National Laboratory

The relationship between atmospheric aerosols and the formation of clouds is among the most uncertain aspects in our current understanding of climate change. Especially, ice and mixed-phase clouds have been less studied even though they have extensive global coverage and dominate precipitation formation. As a result, the climatic impact of ice-containing clouds is not well-understood and there is urgent need to improve ice nucleation formulations in climate models. In order to understand this phenomenon, ice nucleation experiments and parameterization development need to be carried out. Specifically, heterogeneous ice nucleation processes are sensitive to surface properties of atmospheric aerosols, which can accumulate sulfates and organics during atmospheric transport. Thus, here we investigated the physical and chemical properties on the surface of a mixed mineral dust aerosol: Arizona test dust (ATD) and kaolinite mineral dust aerosol particles that trigger ice formation.

In this study, bare and sulfuric acid coated ATD and kaolinite particles were characterized using advanced spectroscopy and microscopy techniques. These particles were reacted with sulfuric acid with different strengths in a systematic way to obtain uniform coatings on the particle surface. Following the acid reaction, the surface composition, chemical state, and elemental mapping of ATD and kaolinite particles were studied using X-ray photoelectron spectroscopy (XPS) and XPS imaging techniques. XPS showed significant changes in composition, chemical state, and elemental distribution of Si and Al on the surface of ATD and kaolinite particles due to the acid reaction. These surface properties also depend on the strength and pH value of the sulfuric acid. The surface morphology, particle size and distribution, and composition of these samples were further studied using scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS). The high resolution SEM micrographs showed differences in surface morphology between bare and coated samples. X-ray diffraction was also carried out to study the changes in crystallinity of ATD and kaolinite particles due to the acid coating. The samples were further characterized using atom probe tomography and transmission electron microscopy to understand the 3-D chemical distribution and microstructure, respectively. Following the characterization of physiochemical properties, ice-nucleation experiments were also carried out on ATD and kaolinite samples, which will be discussed here.

5:20pm **AS+MC+SS-TuA10 A Study of the Effect of Deep UV (172nm) Irradiation on Polyimide Surfaces**, ***Lopamudra Das***, *M.J. Kelley*, The College of William and Mary

Polyimides have a wide range of industrial and scientific applications where changes in surface structure due to UV radiation are of significant interest. Particularly in its use in spacecraft, the effect of deep UV is important to predict photo-degradation of the material. We investigated the response of commercial samples of PMDA-ODA (PI) films to 172nm UV from a xenon excimer lamp in the absence of oxygen, using XPS, ToF/SIMS, and AFM.

5:40pm **AS+MC+SS-TuA11 Small-Angle/Wide-Angle X-ray Scattering Investigation of Functional Materials at Inorganic-Macromolecular Interfaces**, ***Ich Tran***, *T.W. van Buuren, T.M. Willey, J.R.I. Lee, M. Bagge-Hansen, A. Noy, R. Tunuguntla, K. Kim*, Lawrence Livermore National Laboratory

Development in nanoscale engineering has enabled bioelectronics that can mimic and/or interact with the biological systems. Lipid bilayer-functionalized Si nanowires are considered as a promising candidate for the construction of bio-nanoelectronic devices. These biomimetic lipid bilayers serve as a general host matrix for bio-functional components such as membrane proteins. Though meaningful technological advancements have been made, critical questions still remain, in particular on structural characteristics of lipid bilayers at the interface with inorganic nanomaterials. Small-angle and wide-angle x-ray scattering (SAXS/WAXS) techniques are used to investigate self-organizations of dioleoyl-phosphatidylcholine (DOPC) lipid bilayers on Si nanowires. Critical structural parameters of the lipid bilayers (lamellarity, bilayer thickness and packing order of lipid molecules) are obtained through analyzing SAXS-derived Electron Density Profile (EDP). A decrease in bilayer thickness and a packing disorder of the lipid head groups in adjacent to supported Si nanowires have been observed upon coating on Si nanowires. Furthermore, effects on the packing order of lipid hydrocarbon tails induced by the incorporations of proteins or carbon nanotubes into lipid bilayers (served as natural or artificial ion channels, respectively) have been identified and characterized. The results shed light on a number of unresolved questions that are crucial for the comprehensive understanding this class of materials.

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-TuA

Environmental Electron Microscopies
Moderator: Jorge Boscoboinik, Brookhaven National Laboratory

2:20pm **IS+AS+MC+SS-TuA1 Nanocrystal Shape Evolution during Growth**, ***Haimei Zheng***, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

An understanding of nanocrystal shape control mechanisms during growth is critical for the design of novel functional materials with surface-enhanced properties. However, the atomic level shape evolution of nanocrystals during growth is mostly unknown due to the lack of direct observation. We use liquid cells under transmission electron microscope (TEM) to study the growth of Pt or Pt-alloy nanoparticles in situ, where growth either by nanoparticle attachment or by monomer attachment has been observed. First, I will present Pt-Fe nanorods formation by shape-directed nanoparticle attachment under the electron beam. Winding polycrystalline nanoparticle chains are achieved at the early stage then they are straightened to yield single-crystal nanorods. Tracking their growth trajectories allows us to distinguish the force fields exerted by single nanoparticles and nanoparticle chains. Second, I will show the observation of platinum nanocube growth and the facet development. By in situ imaging with high spatial and temporal resolution, we have identified unique growth mechanisms that cannot be predicted by Wulff construction or other existing growth theorems. We found layer-by-layer growth of the {100} and {111} facets while the {110} facets show steps. We also found that the growth rates of these facets are similar until the {100} facets stop growth. Hence, the distance from {100} facets to the crystal center is fixed throughout the subsequent growth. The {110} facets are eliminated when two adjacent {100} facets meet. Lastly, the growth of {111} facets fills the corners to complete a nanocube. Our calculation suggests oleylamine ligand mobility on the facet is responsible for the arresting of {100} growing facets. References:

1. Liao et al. ¬"Facet Development during Platinum Nanocube Gro¬¬wth" Science in review.

2 . H. G. Liao, L. Cui, S. Whitelam, H. Zheng, "Real time imaging Pt3Fe nanorod growth in solution." Science 336, 1011 (2012).

3. We used TEM facility at National Center for Electron Microscopy of Lawrence Berkeley National Laboratory (LBNL), which is supported by the Office of Basic Energy Sciences, Division of Materials Sciences and Engineering of the U.S. Department of Energy under Contract #DE-AC02-05CH11231. H.Z. thanks the support of DOE Office of Science Early Career Research Program.

3:00pm **IS+AS+MC+SS-TuA3 Microfluidic Cell for *In Situ* Scanning Electron Microscopy of Hydrated Dynamic Systems**, ***Christopher Brown***, *A. Yulaev, A. Kolmakov*, National Institute of Standards and Technology (NIST)

The ability to conduct nanoscale imaging of fluid hydrated dynamic systems is a long sought goal within the scientific community. While improvement of commercial instrumentation and environmental cells has enabled in situ imaging of fluid hydrated systems using transmission electron microscopy (TEM) at the nanoscale, additional opportunities exist in implementing in situ techniques within scanning electron microscopy (SEM) instruments equipped with fluidic cells. Factors that motivate this work include: ubiquity and reduced cost of SEM instrumentation compared to TEM, drastically reduced restrictions on the sample size, and greater flexibility of systems and detectors designed for the SEM compared to TEM.

In this communication we report on development of the microfluidic environmental cell designed for in situ studies of fully hydrated dynamic objects. We describe strategies and experimental results that enable improved in situ imaging using the SEM, including development of electron transparent graphene windowed devices that increase signal-to-noise ratio of images of fluid hydrated objects. Limiting factors of in situ imaging of hydrated samples within the SEM are discussed including radiolysis and decreased electron beam penetration into liquid cells compared to higher acceleration voltage electron microscopy modalities.

3:20pm **IS+AS+MC+SS-TuA4 Liquid Jet –X-ray Photoelectron Spectroscopy and MD Simulations indicate that Li Cations in Aqueous Solutions Exhibit High Surface Propensity**, ***Kathryn Perrine***, *M.H.C. Van Spyk, M.J. Makowski, A.C. Stern, K. Parry, D.J. Tobias,* University of California Irvine, *A. Shavorskiy, H. Bluhm,* Lawrence Berkeley National Laboratory, *B. Winter,* Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *J.C. Hemminger*, University of California Irvine

Ions impact chemistry at the aqueous liquid/vapor interface in environmental chemistry, electrochemistry and biomolecular chemistry. Ions are characterized as structure makers or breakers for protein mixtures, and the trend is known as the Hofmeister series.[1] The Born electrostatic model of ions at interfaces has shown that ions should be repelled from the liquid/vapor interface due to a decrease in free energy when solvation by water occurs.[2] Molecular dynamic (MD) simulations and recent experimental studies have shown that anions tend to adsorb to the liquid interface in an inverse Hofmeister trend.[3, 4] Our synchrotron based XPS studies carried out over the last five years have provided experimental evidence that most cations follow classical ionic solution behavior and are repelled from the liquid/vapor interface, whereas some anions exhibit significant propensity for the surface. In this talk we present our recent experiments on Li salt solutions. Our experiments indicate that unlike larger cations, Li^+ is not repelled from the interface and has a significant surface propensity.

Liquid jet-X-ray photoelectron spectroscopy (LJ-XPS) is used to explore the relative ion concentrations at different depths in aqueous salt solutions. Low photoelectron kinetic energies are used to probe the surface of solutions yielding relative ionic concentrations that are present at the liquid/vapor interface. Higher photoelectron kinetic energies probe deeper into the bulk of aqueous solutions. The relative ionic concentrations of solutions prepared from lithium halide salts are compared to potassium halide solutions at different depths. MD simulations support our studies and suggest that Li^+ cations have interfacial propensity due to factors such as the tight water solvation shell on the Li^+ ions. Density profiles reveal anion and Li^+ ion adsorption to the liquid/vapor interface. In addition, we also compare various concentrations of KI and LiI aqueous solutions to determine ion adsorption at the aqueous interface.

1. K. D. Collins and M. W. Washabaugh, *Quarterly Reviews of Biophysics*, 1985, **18**, 323-422.

2. M. Born, *Zeitschrift Fur Physik*, 1920, **1**, 45-48.

3. P. Jungwirth and D. J. Tobias, *Journal of Physical Chemistry B*, 2002, **106**, 6361-6373.

4. D. J. Tobias, A. C. Stern, M. D. Baer, Y. Levin and C. J. Mundy, *Annual Review of Physical Chemistry, Vol 64*, 2013, **64**, 339-359.

4:20pm **IS+AS+MC+SS-TuA7 Complementary Microscopy and Spectroscopy Investigations of the Initial Oxidation Stages of Binary Alloy Thin Films**, ***Judith Yang***, University of Pittsburgh **INVITED**

The transient stages of oxidation – from the nucleation of the metal oxide to the formation of the thermodynamically stable oxide – represent a scientifically challenging and technologically important terra incognito. These issues can only be understood through detailed study of the relevant microscopic processes at the appropriate length scale in situ. We are studying the dynamics of the initial and transient oxidation stages of a metal and alloys with complementary in situ methods - ultra-high vacuum (UHV) transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). We have previously demonstrated that the formation of epitaxial Cu2O islands during the transient oxidation of Cu and Cu-Au thin films bear a striking resemblance to heteroepitaxy, where the initial stages of growth are dominated by oxygen surface diffusion and strain impacts the evolution of the oxide morphologies. We are presently investigating the early stages of oxidation of binary alloys where both elements compete to oxidize. Specifically, we are studying Cu-Ni and Ni-Cr single crystal thin films as a function of relative concentration, oxygen partial pressures and temperatures. For Cu-Ni oxidation, the addition of Ni causes the formation Cu2O and/or NiO where the oxide type(s) and the relative orientation with the film depend on the Ni concentration, oxygen partial pressure and temperature. For Ni-Cr model alloys containing 4, 8 and 16 at.% Cr and isothermally oxidized at 600°C and 10-7 to 10-3 torr O2 pressure, our XPS experiments reveal that after 2 min of oxidation only Cr2O3 forms on the surface of all three alloys. However, with further exposure (i.e., 30 min or 2 h), a competitive growth between Cr2O3 and NiO under all the tested conditions is clear. These XPS data are remarkable results, since prior studies reported in the literature suggest that NiO + internal Cr2O3 or NiO/NiCr2O4/Cr2O3+ internal Cr2O3 should form at least for the lower Cr content (4 and 8%) alloys. These experiments will be complemented with electron microscopy of scale cross sections to better understand the competitive nucleation and growth processes as a function of the oxygen partial pressure.

5:00pm **IS+AS+MC+SS-TuA9 Direct Observation of Structure Controlled Carbon Growth by Environmental TEM**, *J. Kling, T.W. Hansen,* ***Jakob Wagner***, Technical University of Denmark **INVITED**

In order to meet the increasing demand of faster and more flexible electronics and optical devices and at the same time decrease the use of the critical metals, carbon based devices are in fast development. Furthermore, the rich resource of carbon element limits the need for recycling and the material supports the friendly environment approach.

Layered carbon structures spanning from graphene to few layered graphite are used for extremely compact devices with outstanding performance [1,2]. A relative cheap and easy way to produce layered carbon structures on the large scale is via chemical vapor deposition (CVD) growth on catalysts like copper and nickel. However, the exact growth mechanism is still under debate and is most likely dependent on precursor pressure and growth temperature.

Here, we have used environmental transmission electron microscopy (ETEM) to follow the growth of layered structures directly at the atomic level and thereby coupling growth rate and quality of the material on the local scale to the growth parameters. Acetylene and methane are exposed to the catalyst (Ni or Cu) in situ in the microscope at pressures ranging from 0.1Pa 100Pa at temperatures ranging from 500-700C. Following the subsequent appearance of carbon layers allows for determination of instant growth rates under controlled conditions.

Single walled carbon nanotube (SWCNT) based electronics is another way of addressing the environment friendly approach of faster and better electronics. In order to exploit the potential of SWCNTs in the electronic industry fully, selective growth of either conducting or semiconducting tubes is of high importance. Growing the tubes in situ in the ETEM under relevant growth conditions gives fundamental insight in the parameters controlling the chirality and thereby the electronic properties of the SWCNTs.

References:

[1] K. S. Novoselov, S. V. Morozov, T. M. G. Mohinddin, L. a. Ponomarenko, D. C. Elias, R. Yang, I. I. Barbolina, P. Blake, T. J. Booth, D. Jiang, J. Giesbers, E. W. Hill, and a. K. Geim, Phys. Status Solidi **244**, 4106 (2007).

[2] F. Schwierz, Proc. IEEE **101**, 1567 (2013).

5:40pm **IS+AS+MC+SS-TuA11 *In Situ* Energy Loss Spectroscopy, A Novel Approach to the Characterization of Surfaces during MBE Growth**, ***Philippe Staib***, Staib Instruments, Inc.

A new energy analyzer for Auger Electron Spectroscopy (AES), the Auger Probe, is able to operate in growth vacuum chambers to measure *in-situ during growth* the composition of the surface [1,2,3]. The primary beam is provided by the RHEED electron gun at a very grazing incidence angle (2 to 3 degrees). The analyzer is also used in EELS mode to measure Characteristic Energy Losses (CEL). The use of a grazing incidence angle strongly enhances the strength of the energy losses peaks, which become more prominent than the elastic line

EELS data from the Auger Probe are presented showing the evolution of the CEL distributions during oxidation (ZnO), during thermal de-oxidation of GaSb, and during growth of binary and ternary materials (GaAsSb). Surprisingly, even during deposition of homoepitaxial layer, the CEL distribu tions show a marked dependence upon the flux of material to the sample which can reflect the formation of physi- rather than chemisorbed layers and the smoothness of the surface [4].

The CEL spectra cannot be interpreted simply, due to the strong overlapping of multiple excitations of single energy losses. A model is presented that takes into account the probability distribution for multiple losses, and allows extraction of the el ementary energy loss lines from the distribution. Using this model, ac curate energy loss values can be measured and an effective electron density can be calculated. The intensity of the extracted energy losses versus the intensity of the elastic peak is a measure of the ratio d/ l between the electron path length d and mean inelastic free path l of the specific loss. The inelastic mean free path for each loss line can be deducted using d values from monte-carlo simulation of the electron trajectories and the intensity ratio of the loss peak vs. elastic peak.

Special thanks to S. Svensson and W. Sarney of ARL for their collaboration during measurements used in this work.

This work is funded in part by ARO (STTR Phase I - W911NF-13-P-0021A13A-011-0305).

[1] P. Staib, J. Vac. Sci. Technol. B 29(3), (2011).

[2] W.L. Calley, et al. J. Vac. Sci. Technol. B, (2013).

[3] P. Staib in "*In situ* Characterization of Thin Film Growth", Edited by G. Koster and G. Rijnders, Woodhead Publishing In Materials, (2011)

[4] Strawbridge B., Shinh RK.,Beach C.,Mahajan S., Newman N., J. Vac. Sci. Technol. A 24 (5) 1776 (2006) .

6:00pm **IS+AS+MC+SS-TuA12 Selective Staining for Enhanced Spectroscopic Identification of Domains in Immiscible Polymer Blends by Micro-Raman Spectroscopy**, ***Nicholas Heller***, *C.R. Clayton,* SUNY Stony Brook, *S.L. Giles, J.H. Wynne,* Naval Research Laboratory, *M.J. Wytiaz, M.E. Walker*, Sherwin-Williams Company

Blends of incompatible polymers combined with fillers and pigments were used to produce unique low reflectance thermoset coatings. Understanding the origins of low reflectance from the coatings was approached through microscopy, thermal analysis and spectroscopic analysis of both pigmented and control clear coatings. Polymeric phase separation was confirmed by the presence of two distinct glass transition temperatures. Microscopy revealed random surface features for the pigmented coatings. Therefore, the pigments and fillers were removed to observe the polymer-polymer interactions within the blend under curing conditions. Identification of the polymeric domains was obtained using Raman spectroscopy mapping of cross-section samples embedded within a polyester resin. Cross-section samples of coatings were utilized to isolate encapsulated polymer domains from the continuous polymer network to minimize spectral averaging from both domains. Raman analysis of the blends was compared to cured films generated using the individual resins. The embedding process produced a marker peak in one phase and in one individual resin. The marker peak was found to be from styrene monomer and was found to selectively bind to one component of the polymer blend, based on polar and hydrogen bonding characteristics..

Materials Characterization in the Semiconductor Industry Focus Topic
Room: Hall D - Session MC-TuP

Poster Session for all areas of Materials Characterization in the Semiconductor Industry

MC-TuP1 Volumetric and Surface Chemistry of SF_6/C_4F_8/Ar Gas Mixture, ***Robert Bates**, M.J. Goeckner, P.L.S. Thamban, L.J. Overzet*, University of Texas at Dallas

While plasmas using mixtures of SF_6, C_4F_8 and Ar are widely used in deep silicon etching, very few studies have linked the discharge parameters to etching results. We measured the optical emission intensities of lines from Ar, F, S, SF_x, CF_2, C_2, C_3 and CS as a function of the percentage C_4F_8 in the gas flow, the total gas flow rate and the bias power. In addition, the ion current density and electron temperature were measured using a floating Langmuir Probe. For comparison, trenches were etched of various widths and the trench profiles were measured. The addition of C_4F_8 to an SF_6/Ar plasma acts to reduce the availability of F as well as increase the deposition of passivation film. Sulfur combines with carbon in the plasma efficiently to create a large optical emission of CS and suppress optical emissions from C_2 and C_3. At low fractional flows of C_4F_8, the etch process appears to be controlled by the ion flux more so than by the F density. At large C_4F_8 fractional flows the etch process appears to be controlled more by the F density than by the ion flux or deposition rate of passivation film. CF_2 and C_2 do not appear to cause deposition from the plasma, but CS and other carbon containing molecules as well as ions do.

Financial Support Acknowledgement: TI/SRC Award #2261.001

MC-TuP3 SIMS Measurements of Impurities and Alloying Elements in Cu Films used for BEOL Processes, ***Steven Novak**, T. Laursen,* SUNY College of Nanoscale Science and Engineering*, M. Rizzolo,* IBM Albany Nanotech Center*, B. O'brien*, SUNY College of Nanoscale Science and Engineering

Significant recent work has concentrated on the impurity contents of electroplated copper and how they affect the crystallization of copper interconnects. Plating bath additives cause elevated impurity contents in electroplated Cu films that have been thought to pin grain boundaries and strongly affect the recrystallized grain structure of the Cu. SIMS is among the most utilized technique to measure impurity contents in electrochemically deposited Cu however SIMS data is typically only given as relative comparative data. We present quantitative measurements for C, O, S and Cl contents in ECD Cu using both TOF-SIMS (IonTof V) and quadrupole (Phi 6650) SIMS instruments. Using ion-implanted standards we have found that detection limits for impurity elements are typically well below the required limit for ECD Cu. Detection limits are typically one order of magnitude lower using dynamic SIMS compared to TOF-SIMS. The high mass resolution available for TOF-SIMS allows unambiguous quantitative measurement of impurities like S, which experiences mass interference from the O2 molecular ion. Quantitative SIMS analyses show linear increases in impurity contents within plated Cu films as the additive content increases in the plating bath. Although impurity elements are commonly cited as a major effect on the grain size of recrystallized Cu films, recent experiments with intentionally layered Cu samples, having impurity content differences of 2-3X, show that the impurity content has little effect on ultimate crystallite size. Impurity measurements in Cu trenches have been a goal for SIMS for some time. Ion imaging of Cu trenches 450-35nm wide has been carried out using the Bi LMIG gun of the IonTOF V instrument. This instrument is capable of 200nm image resolution. Depth profile analysis of Cu trenches show higher impurity contents within clearly-resolved 450nm wide trenches and suggest even higher contents within smaller trenches, when compared to the Cu overburden. Detection limits in image mode are at least one order of magnitude higher than standard depth profile mode. Alloying Cu with other metals has been proposed as a means of minimizing electromigration within plated Cu lines. Presently Mn is used as an alloy element in seed Cu layers. In addition to Mn, we have studied ion implants of Ag, Co and Ni in Cu as standards for quantifying these elements in seed Cu layers. The alloying element will be present below 1 at percent, less than can be reliably measure with other surface analytical techniques. SIMS analytical methodology and detection limits will be presented for each of these elements in Cu.

MC-TuP4 Growth and Characterization of β-Tungsten Films, ***Avyaya Jayanthinarasimham**, M. Medikonda, A. Matsubayashi, A.C. Diebold, R. Matyi, V.P. LaBella,* SUNY Albany*, P. Khare, H. Chong*, College of Nanoscale Science and Engineering

The giant spin Hall effect (GSHE) is caused by spin orbit interactions in a semiconductor [1] or metal [2] that result in a spin current that is transverse to charge current. Recent spin Hall effect studies in the beta phase of metals such as Ta and W produce transverse spin currents strong enough to switch an adjacent magnetic layer [3]

The metastable β-W is known to exhibit giant spin Hall effect [8]. Deposition conditions selective to β phase of W need to be understood for the large scale fabrication of devices that utilize GSHE. The growth of α and β phases of Tungsten are strongly governed by thickness [4], base pressure [5] and oxygen availability [6] [7]..

This poster will present our work on fabricating and characterizing tungsten films, dominated by the β-phase over a large thickness range by adjusting the oxygen content during the growth. Resistivity measurements as well as x-ray photoelectron spectroscopy and x-ray analysis are performed to determine the phase of the tungsten films.

Reference:

[1] Dyakonov, M.I.Perel, V.I.: Phys. Lett. A 35, 459 (1971)

[2] J.E. Hirsch, arXiv:cond-mat/9906160

[3] Luaiao Liu et al. Science 336, 555 (2012)

[4] D. Choi, et al. J. Vac Sci. Technol.A 29, 051512 9 (2011)

[5] S.M. Rossnagel et al. J.Vac. Sci. Technol. B20, 2047 (2002)

[6] S.Basavaiah Appl. Phys. Lett. 12, 259 (1968)

[7] T. Karabacak et al. Thin Solid Films 493 (2005) 293-293

[8] C.F.Pai et al. [http://arxiv.org/abs/1208.1711]

MC-TuP6 Some Experience in Characterizing Thin Films on Next Generation 450mm Wafer with Spectroscopic Ellipsometry, ***Richard Sun**, N. Sun*, Angstrom Sun Technologies Inc.

Under guidance of International SEMATECH Manufacturing Initiative(ISMI), Angstrom Sun Technologies Inc developed the first tabletop spectroscopic ellipsometer for 450mm wafer application. A few challenges regarding wafer handling and small edge exclusion requirement will be discussed. With improved modeling, spectroscopic ellipsometry could also be used to determine EBR profile of photoresist by linear line scan near the wafer edge.

MC-TuP7 The Effect of Aberration Coefficients on Phase Shift in Electronic Optics, ***Chien-Nan Hsiao**, J.S. Kao, F.Z. Chen, J.L.A. Yeh*, ITRC, NARL, Taiwan, Republic of China

The epitaxial SiGe/Simultiple quantum wells (MQWs) were grown by ultra-high vacuum chemical vapor deposition (UHV-CVD) on a single crystalline silicon (111) substrate. Aberration corrected scanning transmittance electron microscopy equipped the high bright electron gun, DCOR aberration corrector, high angle annular dark field (HAADF) detector, and EDS was used to analysis the atomic structure of SiGe/Si interface. The defocus (C1) and aberration coefficients of electronic optics system such as astigmatism (A1, A2, A3, A5), coma (B2, B4), spherical aberration (C3, C5), and star aberration (S3) were corrected preciously by changing the convergence angle of electron beam probe (18 and 25 mrad). It was found that the distance between dumbbell Si and Ge atoms could be directly measured by the HRSTEM HAADF image. The corresponding FFT shows the point resolution was shown higher point resolution. In addition, the effect of aberration coefficients on phase shift in electronic optic (phase plate) was investigated. Furthermore, the experimental results also demonstrated that simultaneously complementary atomic-resolution EDS line-scan signal in HRSTEM HAADF image. These results provide an effective approach to investigate structural chemical element image in real space at the atomic resolution.

MC-TuP8 Modification of Density of States in Iron Chloride Intercalated Epitaxial Graphene with Electric Bias, ***Taurean Groover**, M.D. Williams*, Clark Atlanta University

Graphene, an atomic thick layer of carbon in a hexagonal lattice, has received a large amount of attention from researchers across many different scientific disciplines. Within the condensed matter physics community it is fairly well agreed that the electronic, optical, as well as structural properties of graphene are poised to revolutionize the semiconductor industry. This unique collection of properties proves promising but there are some

obstacles that need to be addressed before these properties can be fully exploited. Graphene is a semimetal, which means that the conduction and valence bands touch at the Dirac point leaving no band gap to be utilized in semiconductor and optoelectronic devices. In this work we seek to investigate the electronic characteristics of epitaxial graphene, stage one and stage three ferric(III) chloride intercalated epitaxial graphene. We investigate the opening of a band gap in graphene through intercalation and in conjunction with the application of an appropriate electrical bias normal to the sample surface. Through theoretical calculations, we show that the electrical bias normal to the surface not only tunes the carrier concentration but also has the ability to switch the majority carriers from electrons to holes. The Walt de Heer Confinement Controlled Sublimation method was employed for the production of the epitaxial graphene samples and the two zone vapor transport method was employed for the intercalation of the samples. With the Confinement Controlled Sublimation growth method used, graphene is grown on SiC substrates which make these materials uniquely suited for a smooth integration into existing silicon based electronics. We observe, compare, and interpret the alteration of the density of states as well as the work functions of these samples upon the application of the electric field normal to the sample surface. Analyzing the band structure of these samples, we witness a change of the band structure from that of the AB stacking configuration to that of the decoupled AA stacking configuration. In conjunction with Raman spectroscopy, this confirms the electronic decoupling of graphene layers. Auger spectroscopy was employed to investigate the chemical environment of the near surface region of the samples and may be a viable method for stage number determination in intercalated materials. When intercalated with $FeCl_3$, the optical transparency of the sample is conserved and the resistivity drops tremendously which makes this material, in particular, uniquely suited for the production of transparent electrodes that can be utilized to improve the performance of Li-Ion batteries.

Applied Surface Science
Room: 316 - Session AS+BI+MC-WeM

Chemical Imaging in 2D and 3D
Moderator: Jeffrey Fenton, Medtronic, Inc., Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

8:20am **AS+BI+MC-WeM2 Expanded Approaches for Single Cell Analysis by SIMS**, ***Christopher Szakal***, National Institute of Standards and Technology (NIST)

Secondary ion mass spectrometry (SIMS) has been increasingly utilized for single cell imaging owing to its unique combination of spatial resolution and chemical differentiation by mass. Depending on the instrument type, subcellular lateral resolution between 10's and 100's of nanometers can be obtained, sometimes with both elemental and organic information obtained simultaneously, and sometimes with highly precise isotopic ratio measurements being attainable. However, imaging at the limits of the technique requires sufficient counts per pixel, which can be limited by analyte concentrations, competitive ionization pathways, and cumulative cluster ion beam damage accumulation. This work focuses on the advantages and disadvantages of combining focused ion beam (FIB) milling of single cells with subsequent ToF-SIMS imaging, as well as using large geometry (LG)-SIMS for high mass resolution analysis of single cell components that would otherwise not be easily detectable in other instrumental configurations. Such developments expand the research areas that are possible for single cell SIMS analyses, including cell differentiation without relying on multivariate analyses and targeted cell uptake studies.

8:40am **AS+BI+MC-WeM3 3-Dimensional Chemical Imaging on the Nanoscale with Cluster-SIMS**, ***Nicholas Winograd***, Penn State University **INVITED**

Bombardment of molecular solids with polyatomic projectiles allows interrogation of the sample with reduced chemical damage accumulation. Hence, it is now possible to perform depth profiling experiments with a depth resolution of less than 10 nm. In our hands, the projectile of choice is C_{60} due to the fact that the ion beam can be focused to a 250 nm spot size, and erosion of the sample can be performed with minimal chemical damage, especially at low temperature. With this combination of properties, it is feasible to think about creating 3-dimensional molecule-specific images.

A basic impediment to accomplishing this goal involves the fact that the SIMS images provide only chemical information and no direct depth information. The measureable quantity is the incident ion beam fluence, which can indirectly be related to depth, but independent measurements are required. The formation of topography and differential sputtering effects across the sample surface can also degrade the quality of the 3-D rendering when 2-D images are stacked. We have employed AFM in combination with SIMS imaging to develop protocols for correcting for these phenomena. Here, examples are shown using a patterned trehalose thin film and an Irganox delta layer reference material provided by NPL in the U.K. The idea is to provide chemical information with SIMS, and the depth information, acquired at each pixel in the image, using AFM. In addition to examining eroded craters directly, we have also developed a wedge-beveling technique that allows sputtering yield and topography to be determined with a single SIMS measurement and a single AFM measurement.

The long term aim of developing these protocols is to be able to acquire high resolution chemical images of single biological cells. So far, it appears that differential sputtering effects are not too serious for these samples. The combined SIMS/AFM strategy developed here will be important for verifying these initial observations. Finally, there is an emerging interest in gas cluster ion sources, namely Ar_{4000}, since even less chemical damage than C_{60} is observed, and the depth resolution during erosion appears to be less than 5 nm. Here we show that the combination of C_{60} imaging and Ar_{4000} sputtering provides an even more powerful protocol. In general, we show that the AFM/SIMS combination is a powerful tool for 3-dimensional chemical imaging.

9:20am **AS+BI+MC-WeM5 SIMS 2D and 3D Characterization of Organic/Inorganic Surfaces by FIB Crater Wall Imaging and Tomography**, ***Felix Kollmer***, *R. Möllers, D. Rading, S. Kayser,* ION-TOF GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *E. Niehuis*, ION-TOF GmbH, Germany

Information on the chemical composition, physical properties and the three dimensional structure of materials and devices is of major importance. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is known to be an extremely sensitive surface imaging technique which provides elemental as well as comprehensive molecular information on all types of solid surfaces. In the so-called dual beam mode the pulsed analysis beam is combined with a low energy sputter ion beam for the removal of material. This allows depth profiling of multilayers with high depth resolution as well as three-dimensional analysis.

However, the analysis of structures at greater depth (> 10µm) requires long measurement times and the build-up of surface roughness at the crater bottom limits the achievable spatial resolution. Moreover, extremely rough samples, samples with voids, and material that exhibits strong local variations in density or sputter yield are unsuitable for conventional depth profiling. Not only that the initial surface topography is unknown but it is also modified and in many cases even roughened by the sputtering process.

In order to overcome these limitations we used a combined SIMS/FIB setup. Either a Bi cluster beam or a mono-atomic Ga beam is used to FIB mill a crater into the sample. Subsequently, a 2D TOF-SIMS image of the vertical crater wall is acquired. Since the crater wall is hardly affected by the aforementioned roughening problems this approach allows the in-depth distribution of elements to be determined by analyzing a plane perpendicular to the surface at high lateral resolution (Dl<50nm) [1].

Moreover, by serial slicing of the crater wall followed by intermediate analysis steps this approach can be extended in order to provide the full 3D characterization of the analyzed volume. We will present 2D and 3D data of reference material, multilayer samples and technically relevant real world samples such as fuel cells and battery electrodes. For thin multilayer samples the FIB process can be performed under grazing incidence in order to bevel the surface and hence magnify and accentuate thin layers in the plane of the analyzed crater wall.

However, the FIB/SIMS approach fails when analyzing organic surfaces since the molecular structure is almost completely destroyed by the sputtering process. We will discuss methods to maintain the molecular structure under high dose sputtering conditions by performing the FIB milling with massive argon clusters.

[1] F. Kollmer, W. Paul, M. Krehl, E. Niehuis, SIMS XVIII proceedings paper, Surf. Interface Anal., 2012

9:40am **AS+BI+MC-WeM6 Multivariate Imaging: A New Approach towards Chemical State Identification of Novel Carbons in XPS Imaging**, ***Anders Barlow***, *N. Sano, P.J. Cumpson*, NEXUS, Newcastle University, UK

The differentiation between various forms of carbon in XPS spectra is made difficult by the subtle changes in C1s spectra that one would typically analyse. This is ideally demonstrated by a comparison of sp^2 and sp^3 carbon, such as graphite and diamond, where the variation in the C1s peak is less than 1eV. When applied to 'real' samples, such as a diamond like carbon coating, or a graphene surface, this difference can be even less. This presents a real problem for XPS imaging, where typically the analyst would sacrifice energy resolution in favour of signal intensity and spatial resolution. Such subtle differences are then completely lost when performing XPS imaging of novel carbon surfaces, where there may be discrete boundaries or layers between materials that are chemically very different, yet appear the same when the C1s peak energy is used in imaging.

We report a method of elucidating these differences in XPS imaging through shifting the focus from the C1s feature, to the X-ray induced Auger feature, a method we call Multivariate Auger Feature Imaging (MAFI). The carbon Auger feature can be studied and through the extraction of the so-called D-Parameter[1], chemical states of carbon can be clearly identified, with little ambiguity between sp^2 and sp^3 states. Extension of this method to XPS imaging, and the generation of 3-Dimensional images (2 spatial, 1 kinetic energy), we have shown that imaging of the Auger feature of graphite on polymers can identify multiple states of carbon-carbon bonding domains, where the imaging of the C1s feature alone yields no distinguishable differences or spatial features. We have also shown that PCA analysis of the carbon Auger feature also yields clear and distinguishable differences in the XPS images. The result is two independent methods of distinguishing novel carbon materials from one-another in XPS imaging. With modern instrumentation capable of a spatial

resolution down to the few micron level, this greatly enhances the capability of XPS instrumentation to image novel carbon surfaces and devices.

[1] Lascovich, J.C. et al., App. Surf. Sci., 47(1), pp. 17-21 (1991).

11:00am **AS+BI+MC-WeM10 Multivariate Analysis Approaches for Image De-noising and Image Fusion**, ***Bonnie Tyler***, National Physical Laboratory (NPL), UK **INVITED**

Image fusion has become widely used in both medical diagnostics and optical remote sensing and there is growing interest in using these methods in applied surface science research. The goal of data fusion is to combine measurements from complementary techniques in order to aid in the analysis of the data and enhance information content. Recently, pan-sharpening techniques developed for optical remote sensing have received considerable interest in the surface science community because of their ability to improve spatial resolution and image contrast. Although image fusion can produce dramatic improvements in image sharpness and contrast, it can also lead to significant artefacts and care must be taken to ensure reliable results. These artefacts can be quite severe if the spectra have sharp bands, high background, or low signal-to-noise, features that are common in ToF-SIMS and XPS imaging. For optical remote sensing, a wide variety of methods have been developed for pan-sharpening, including approaches based on wavelet transforms, high pass filters, intensity hue saturation, Gram-Schmidt transforms, and Principal Components Analysis. Each of these methods offers advantages for certain applications but all are prone to artefacts when applied under non-optimal conditions. In order to minimize artefacts and produce reliable results, the methods must be adapted to account for the unique characteristics of different imaging modes. Of the methods in the literature, PCA image fusion is the most readily adapted for use with ToF-SIMS and XPS images. Methods for adapting PCA fusion for optimal use with ToF-SIMS and XPS images will be presented, including statistically based preprocessing of the data, target factor rotations and histogram matching. PCA image fusion can be a valuable technique for reducing noise, improving image contrast, and spatial resolution in ToF-SIMS and XPS data. With appropriate attention to the unique characteristics of each spectrometry, this can be done without significant artefacts or distortion of the spectral detail.

11:40am **AS+BI+MC-WeM12 Global Analysis Peak Fitting for Imaging NEXAFS Data**, ***Mark H. Van Benthem***, *J.A. Ohlhausen*, Sandia National Laboratory

We will present a method of analyzing NEXAFS image data to extract chemical information from the complex elemental peak structure in the material under analysis. The method, known as global analysis, fits emission bands to peaks described by nonlinear functions using nonlinear and linear optimization techniques. It can fit multiple types of peaks simultaneously, such as those found in NEXAFS spectra: Gaussian, Lorentzian, Voigt, asymmetric Gaussian and Lorentzian, and step edge with decay. Typically, peak fitting of NEXAFS data is very complex and somewhat arbitrary. Our method takes advantage of the high dimensionality of the image space to yield peaks with potentially greater reliability than single spectrum fitting. The method also employs data compression with principal component analysis (PCA) to rapidly complete the analysis. A discussion of the algorithm along with several examples of its application will be presented.

Sandia is a multiprogram laboratory 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.

12:00pm **AS+BI+MC-WeM13 Visualizing Pharmaceutical Compounds in Single-cells with label-free 3D Mass Spectrometry Imaging**, ***Melissa K. Passarelli***, *C. Newman,* National Physical Laboratory, UK, *A. West,* University of York, UK, *C.T. Dollery, I.S. Gilmore,* National Physical Laboratory, UK, *J. Bunch*, National Physical Laboratory

Drug-induced phospholipidosis is an adverse side-effect that hinders the therapeutic value of some pharmaceutical compounds. In this report, three-dimensional secondary ion mass spectrometry (SIMS) imaging was used to investigate the cellular uptake of phospholipidosis–inducing pharmaceutical compounds. A fast and simple sample preparation method, frozen dehydrated, was used to extract the drug compound to the surface layers of individual cells. Although the native localization of drug compound within the cell is lost, the compound was isolated to the confines of the individual cells and matrix-related effects were no longer a concern. With this method we were able to successfully detect intact-unlabeled drug compound at therapeutic dosages in macrophages. Relative quantification of the drug compound in individual cells was achieved. Overall, this approach provides a platform for studying cellular uptake of pharmaceutical compounds at the single cell level. This system also provides a model for studying metrology of cell imaging using SIMS. The effects of sample preparation and limitations of current technologies will be discussed along with new possibilities for the future.

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+AS+MC+SS-WeM

In-Situ X-ray Absorption and Raman Spectroscopy
Moderator: Hirohito Ogasawara, SLAC National Accelerator Laboratory

8:00am **IS+AS+MC+SS-WeM1 *In Situ* Studies on the Behavior of Metal/Oxide Catalysts during the Water-gas Shift Reaction**, ***Jose Rodriguez***, *D. Stacchiola, S. Senanayake, J. Hanson*, Brookhaven National Laboratory **INVITED**

In this talk, it will be shown how a series of *in-situ* techniques [X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AP-XPS)] can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxide catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, $CO + H_2O \rightarrow H_2 + CO_2$). Under reaction conditions most WGS catalysts undergo chemical transformations that drastically modify their composition with respect to that obtained during the synthesis process. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO_2, TiO_2, CeO_x/TiO_2 and Fe_2O_3 essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. IR and AP-XPS have been used to study the reaction mechanism for the WGS on the metal/oxide catalysts. Data of IR spectroscopy indicate that formate species are not necessarily involved in the main reaction path for the water-gas shift on Cu-, Au- and Pt-based catalysts. Thus, a pure redox mechanism or associative mechanisms that involve either carbonate-like (CO_3, HCO_3) or carboxyl (HOCO) species should be considered. In the last two decades, there have been tremendous advances in our ability to study catalytic materials under reaction conditions and we are moving towards the major goal of fully understanding how the active sites for the production of hydrogen through the WGS actually work.

8:40am **IS+AS+MC+SS-WeM3 Tuning Catalytic Performance of Bimetallic Nanoparticle Catalysts through a Single or Sequential Post-Synthesis Reaction in a Gas Phase**, *F. Tao, J. Shan, S. Zhang, L.T. Nguyen,* University of Notre Dame, *A. Frenkel,* Yeshiva University, *J. Greeley,* Purdue University, ***Shibi Zeng***, University of Notre Dame

Besides a sophisticated synthesis of bimetallic nanocatalysts in a colloidal solution, a post-synthesis reaction in a gaseous phase is a complementary method to tailor the surface structure and composition of a bimetallic nanocatalyst to tune its catalytic performance. Here we illustrate the capability of creating a new catalyst surface exhibiting a lower activation barrier through segregation of a bimetallic catalyst in a post-synthesis reaction in a reactive gaseous environment. In-situ surface chemistry of bimetallic nanocatalysts were analyzed with AP-XPS. Coordination environment of Pt and Cu atoms under different reaction conditions was tracked with in-situ EXAFS. The surface restructuring was simulated with DFT calculation from thermodynamic,ci point of view. The composition and geometric structure of the newly formed surface of the bimetallic nanocatalysts strongly depend on the reactant gas used in the post-synthesis reaction. A further sequential reaction in a different gas after the initial post-synthesis reaction in a gas forms a different catalyst surface. A post-synthesis reaction of a Pt-Cu regular nanocube (Pt-Cu RNC) in hydrogen forms a near surface alloy (NSA) which exhibits an activation barrier of 39 kJ/mol for CO oxidation, much lower than pure Pt nanocubes. These studies demonstrate a method of tuning catalytic performances and generate another catalytic phase through a post-synthesis reaction in a gas phase.

9:00am **IS+AS+MC+SS-WeM4 *In Situ* Characterization of Metal-Based Ionic Liquids using X-ray Spectroscopy**, ***Robert Meulenberg***, University of Maine, *C. Apblett, H. Pratt, T. Anderson*, Sandia National Laboratories

Energy storage for vehicles is advancing rapidly, and one of the possible contenders for a battery that can quickly be recharged is a redox flow battery, which uses liquids that are pumped into the battery to be charged or discharged, and then removed to storage containers. This makes the chemistry roughly analogous to liquid fuels employment, where the charged

chemistry is pumped into the battery, discharged, and then pumped into a waste container, similar to fuel pumped into an engine, ignited, and then expelled through the tailpipe. Unlike internal combustion engines, however, the discharged product is retained on the vehicle, and can be subsequently either recharged on the vehicle, or pumped off the vehicle to be recharged at a filling station, while replacing with freshly charged material.

To date, however, the concentrations of most redox flow battery chemistries have been low, below the 1-2M concentration level. Recently, a new type of ionic liquid (IL) redox flow chemistry has been developed that raises this to 5-6M, and improves the energy density of the system. However, little is known about the structure of the molecule in the charged and discharged states. The current understanding of the structure of the IL, primarily the Fe IL, comes from primarily from FTIR, Raman, and TGA/DSC data, as traditional methods such as NMR to probe surface chemistry are limited due to the paramagnetic Fe center. It is believed the coordination of the ligand to the metal center occurs primarily through the alcohol groups. Cyclic voltammetry of the FeIL exhibits behavior associated with Fe(III)/Fe(II) reduction/oxidation, with some evidence that the ligands are coordinating to adjacent Fe atoms, resulting in antiferromagnetic coupling between the metal centers. A complete, fundamental understanding of the local coordination and ligand environment is not known and is the primary goal of our research. To further understand this structure, we have constructed a new electrochemical cell to be used for *in situ* transmission Fe K-edge x-ray absorption fine structure (XAFS) spectroscopy. We conduct our measurements at various states of charge, and the structure of the molecule in these various states is determined using this from analyzing both the XANES and EXAFS. Effects of electrochemical cell potential on local structure of the FeIL will be discussed.

9:20am **IS+AS+MC+SS-WeM5 Monitoring Catalysts during Catalytic Reactions with *In Situ* Raman Spectroscopy**, ***Israel Wachs***, Lehigh University **INVITED**

The surfaces of heterogeneous catalysts in reactive environments are dynamic and require *in situ* characterization studies under reaction conditions to fully understand their fundamental structure-activity relationships. This presentation will focus on the application of Raman spectroscopy to determine the nature of the catalytic active sites in different reaction environments. Emphasis will be placed on investigating heterogeneous supported metal oxide catalysts containing multiple catalytic active sites and determining the roles of each of the sites. Some of the examples to be presented will be the metathesis of $H_2C=CHCH_3$ to $H_2C=CH_2$ and $H_3C-CH=CHCH_3$ by supported ReO_x/Al_2O_3 catalysts, polymerization of $H_2C=CH_2$ by supported CrO_x/SiO_2 and methane conversion to aromatic liquids by supported MoO_x/ZSM-5 catalysts.

11:00am **IS+AS+MC+SS-WeM10 Photoelectron Spectroscopy on Ice, Mineral Oxides and Aqueous Solutions of Atmospheric Relevance**, ***Markus Ammann***, Paul Scherrer Institut, Switzerland **INVITED**

Aerosol particles and ice are key in atmospheric chemistry as many chemical and physical processes occurring on and within them are relevant for air pollution and climate. The fundamental understanding of these processes increasingly relies on a molecular level description of structures and mechanisms. This requires tools to access condensed phase – air interfaces with structural and chemical selectivity. Recent advances in pushing the pressure limits of ultrahigh-vacuum surface science methods such as photoelectron spectroscopy have allowed the investigation of environmentally relevant surfaces under nearly ambient conditions and have thereby significantly contributed to the advancement of our understanding of interfaces in the atmosphere. In this overview, recent results on the interaction of acidic gases with ice surfaces, of chemical and photochemical processes on mineral oxides, and of the structure of aqueous solution surfaces will be presented. These examples also demonstrate the instrumental requirements for such in situ experiments, and our recent developments of sample environments to facilitate experiments with environmental substrates will be presented.

11:40am **IS+AS+MC+SS-WeM12 *In Situ* Analysis of Materials Under Mechanical Stress: A Novel Instrument for Simultaneous Nanoindentation and Raman Spectroscopy**, ***Chris Michaels***, *Y.B. Gerbig, R.F. Cook*, NIST

Instrumented indentation or “nanoindentation” is a method that is widely used in the study of the mechanical deformation of materials on small length scales (~ micrometer). Raman spectroscopy is a technique that provides insight into the molecular or crystallographic level processes involved in the mechanical deformation of materials, such as strain build-up, phase transformations and variations in crystallinity. Typically these approaches have been used separately wherein the spectroscopic analysis of the material might take place prior to and after the end of a mechanical transformation. Of course, there is significant interest in *in situ* analyses of materials during mechanical transformation as such an approach promises a richer understanding of the underlying physics than is likely possible with analysis limited to pre- and post-transformation. For example, the ability to follow the path of phase transformations rather than just the endpoints is certainly desirable. Consequently, significant effort has been directed toward the coupling of indentation instruments with various in situ analysis capabilities.

This talk describes the design and operation of a nanoindentation instrument that is coupled with a laser scanning Raman microscope to conduct *in situ* spectroscopic analyses of mechanically deformed regions of optically transparent materials under contact loading. The force transducer of the device allows adjustment of crucial experimental parameters, such as indentation loads and loading rates. An incorporated displacement sensor allows for collection of force-displacement curves comparable to conventional nanoindentation instruments. The device is mounted on the sample stage of an inverted optical microscope that is configured for Raman microscopy, allowing optical access to the mechanically deformed regions of transparent samples. The capabilities of this novel instrument will be demonstrated by *in situ* studies of the indentation-induced phase transformations in an epitaxial silicon-on-sapphire (SoS) thin film, in both a microspectroscopy and a laser scanning Raman imaging configuration.

Applied Surface Science
Room: 316 - Session AS+BI+MC-WeA

Practical Surface Analysis I
Moderator: Alexander Shard, National Physical Laboratory, Christopher Szakal, National Institute of Standards and Technology (NIST)

2:20pm **AS+BI+MC-WeA1 The Application of XPS to Study Corroded Stainless Steel Surfaces**, ***Helen Brannon***, *S.J. Coultas, J.D.P. Counsell, S.J. Hutton, A.J. Roberts, C.J. Blomfield,* Kratos Analytical Limited, UK*, J. Morrison*, The University of Birmingham, UK

The corrosion of structural materials in contact with hot, pressurised water, which is heavily dependent on the condition of the exposed surface, is a common problem in nuclear power processes. This side reaction is undesirable due to the reduced heat transfer efficiency which is caused by the deposited oxide layers.

X-ray photoelectron spectroscopy (XPS) is demonstrated as a quantitative surface analysis technique which can be used to determine the type of corrosion chemistry that occurs.

Stainless steel (316L) substrates containing 70% Fe, 18% Cr, 8% Ni and 2% Mo (as well as a low concentration of impurities) are suspended in water at 300 °C for 1000 hours. A metal oxide double layer is found to develop over time on the stainless steel surface: the top layer is a mix of magnetite (Fe_3O_4) and Nickel Ferrite ($NiFe_2O_4$) and the bottom layer is a mix of magnetite and chromite ($FeCr_2O_4$) (below is the base metal).

A high energy, medium sized argon gas cluster source is shown to be advantageous compared to a conventional monatomic argon ion source when depth profiling such layered structures, causing reduced structural and chemical damage from the ion beam sputtering process.

Data acquisition at small analysis areas gives well resolved spectra, revealing the multi-layered oxide structures produced from the corrosion process.

[1] Depth profiling of the Passive Layer on Stainless Steel using Photoelectron Spectroscopy, Wendy Fredrikkson, Uppsala University

[2] Applied Surface Science, 257, (2011), 2717–2730

[3] The Radiochemistry of Nuclear Power Plants with Light Water Reactors, By Kark-Heinz Neeb

2:40pm **AS+BI+MC-WeA2 Molecular Characterization of Lubricant Degradation Produced in a Tribological Wear Test Using TOF-SIMS and Scanned Microprobe XPS Imaging**, ***Gregory Fisher****, S.S. Alnabulsi,* Physical Electronics Inc.*, T. Le Monge,* Ecole Centrale de Lyon - LTDS, France*, J.S. Hammond*, Physical Electronics Inc.

Scanning Auger microscopy (SAM) and x-ray photoelectron spectroscopy (XPS) are today the most widely used surface analysis techniques for quantitative elemental and chemical analysis in tribology. Modern SAM instrumentation allows the elemental and chemical analysis of features at spatial resolutions down to 10 nm while modern scanning x-ray microprobe XPS instrumentation can provide even more complex chemical state surface characterization at a sub-10 µm spatial resolution. The use of a scanned x-ray microprobe enables chemical state imaging at a low x-ray fluence to minimize disturbance of the surface chemistry. Notwithstanding the aforesaid capabilities, the elucidation of molecular chemistry and lubricant degradation that occurs via tribological wear remains intractable by SAM and XPS analysis alone.

This study focuses on the application of time-of-flight SIMS (TOF-SIMS), with supporting XPS analysis for quantification, to determine the molecular decomposition and metal-organic reaction products of lubricants used in bio-diesel fuel. The test specimens were produced on a reciprocating cylinder-on-flat tribometer to simulate the piston / cylinder contact geometry and dynamics that are typical of internal combustion engines. The lubricant used in the bio-diesel fuel consists of C_{18} fatty acids at a concentration in the high part-per-million (ppm) range. The TRIFT mass spectrometer of the PHI *nanoTOF* provides an advantage for this study in that the wear track topography is effectively decoupled from the molecular characterization and imaging. The HR^2 imaging mode of the PHI *nanoTOF*, simultaneously achieving a spatial resolution < 400 nm and a mass resolution of $\approx 10,000$ m/Δm, is an important asset in molecular identification and imaging.

3:00pm **AS+BI+MC-WeA3 Surfaces and Interfaces of Real-World Products: What Do We Really Need to Know and What Are The Best Ways to Find Out?**, ***Anna Belu****, L. LaGoo, W. Theilacker*, Medtronic, Inc. **INVITED**

Real world components and products come in many shapes, sizes and materials, and their surface properties are critical for performance in many areas including adhesion, biocompatibility, corrosion, lubricity, and welding. Surface analysis tools are often employed to gain a fundamental understanding of surface properties of products in development, as well as to evaluate properties of surfaces and interfaces of products that are not performing as specified. This presentation will discuss best practices for analysis of real world samples in an industrial, mainly R&D, environment.

The culture of industry is typically fast paced with the goal being to get product into the hands of consumers as soon as possible. In this environment, the surface analyst is faced with the challenge of providing high quality information from a variety of materials and issues in a short amount of time. The requestor often wants a simple answer and is unaware that the analyst progresses through a series of questions such as What is the issue? What are the best tools to find the answer to the issue? Are the tools up to the task? Is the lab up to the task? What types of results are necessary? What types of samples are helpful? What is the most efficient way to obtain the data? Is it OK to use one tool and analyze one point on one sample? What are efficient ways to analyze data ? Do the results solve the problem? This presentation will discuss the consideration that goes into providing high quality data in a short amount of time and include several examples of surface analysis from real world products.

4:20pm **AS+BI+MC-WeA7 Forensic XPS Surface Characterization of Cosmetic Trace Evidence**, ***Brian Strohmeier****,* Thermo Fisher Scientific*, R. Blackledge*, Independent Consultant

X-ray photoelectron spectroscopy (XPS) has a long distinguished history of providing important information on the surface chemistry of a wide variety of materials including: catalysts, ceramics, coatings, fibers, glass, metals, oxides, polymers, powders, semiconductors, thin films, and many others. In addition, studies involving the use of XPS have addressed numerous complex materials problems in a multitude of diverse fields such as: adhesion science, chemical surface treatments, corrosion, electronics, medical devices, oxidation, solar cells, and so on. Despite its many advantages and unique capabilities as a surface analytical technique, XPS has not been widely used in forensic science for the examination of specimens gathered at the scene of a crime. The main reasons for the lack of forensic studies involving XPS are: 1) the lack of standard forensic XPS methods and standard samples for comparison to real world samples; and 2) the historical long analysis times (hours per sample) and large analysis areas (several square millimeters) compared to other common forensic techniques such as Raman microscopy and scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS). Advances in XPS instrumentation over the last decade have now improved analysis times to minutes per sample and analysis areas down to the range of tens to hundreds of micrometers. Also, recently developed argon cluster ion sources now allow "soft" depth profiling of organic and polymeric species with minimal ion beam damage, thus preserving the chemical state information available from XPS. XPS, therefore, has increased potential for new forensic science applications involving the surface characterization of trace evidence materials. Previous work has demonstrated the potential of XPS for revealing unique surface chemical information for gunshot residue (GSR) and textile fibers. This presentation will describe the use of XPS for forensic characterization of cosmetic materials such as hair chalks, shimmer, and glitter. These types of cosmetic materials have a high probability of transfer and retention if a victim struggles with an assailant during an abduction or sexual assault and could help support an association between an assailant, a victim, and a specific crime scene in a specific case circumstance. XPS is an excellent technique for characterizing residues of these cosmetic materials.

4:40pm **AS+BI+MC-WeA8 Industrial Applications of Surface Analysis**, ***William Stickle****, M.D. Johnson, G.A. DeHaan, J.A. Burgess*, Hewlett Packard

Using surface analysis has been a mainstay of industrial research and corporate analytical labs for more than thirty years. The applications of surface chemical analysis in an industrial setting range from the investigation of the composition and chemistry of buried interfaces of single molecule memory devices created in the R&D lab to the routine analysis of plasma treated polymer surfaces on the production line. Some analyses are performed to provide a 'yes' or 'no' answer to question such as 'Has the oxide been removed?' or 'Was the surface plasma treated?'. Other analyses

are much more complicated and often require the application and correlation of several analytical methods. This correlation between techniques often occurs in the characterization of, for example, fab processes where a process may be characterized by x-ray photoelectron spectroscopy to understand the chemistry; but then the analysis needs to correlate to the information obtained by Auger electron spectroscopy or ToF SIMS which are the techniques of choice when the process is scaled to dimensions where XPS is not practical. Further, simple data processing, such as calculating atomic concentrations, is often not the end of the analytical story. Examples of using numerical methods such as linear least squares fitting or the application of Tougaard backgrounds to clarify an analysis will also be discussed. More detailed analyses can also be achieved by applying modeling methods such as SESSA or using simple overlayer models to describe a material. This presentation will cover these different aspects of surface chemical analysis in an industrial laboratory with practical examples of using XPS, AES and ToF SIMS for process characterization, materials development and failure analysis.

5:00pm **AS+BI+MC-WeA9 Peter Sherwood Mid-Career Award Talk: Chemical Analysis of Cells and Tissues with Imaging ToF-SIMS***, **Lara J. Gamble**, B. Bluestein, D. Graham*, University of Washington **INVITED**

The ability to image cells and tissues with chemical and molecular specificity could revolutionize our understanding of biological processes. It would increase our understanding of chemical changes in cells and tissues as a function of an applied stress or as a result of disease, and enable tracking the spatial distribution of metabolites and lipids. Chemistry of tumor microenvironments, lipid metabolomics relationship to cancer, delivery of nanoparticles to cells, and tissue repair could be visualized on a cellular and sub-cellular level. The sub-cellular resolution mass spectral imaging capability of ToF-SIMS holds the potential to achieve this possibility. ToF-SIMS analysis of biological samples from 2D images of tissue biopsies to 3D images of nanoparticles in cells will be presented including multivariate analysis of the ToF-SIMS image data. The ToF-SIMS images are also combined with optical images of the same samples (same slices and serial biopsy slices). This combination of images allows researchers to visualize a molecular map that correlates with specific biological features or functions. The potential to combine the ToF-SIMS images with other techniques will also be discussed.

5:40pm **AS+BI+MC-WeA11 Characterization Strategies for the Detection of Carbon Nanotubes within an Epoxy Matrix***, **Justin Gorham**, J. Woodcock, W.A. Osborn, J. Heddleston, K. Scott*, National Institute of Standards and Technology (NIST)

Carbon nanotubes (CNT) have been widely incorporated into composite systems due to the enhanced properties that they add to new and existing products, especially with respect to mechanical strength. X-ray photoelectron spectroscopy (XPS), in conjunction with SEM and Raman spectroscopy, has been employed in efforts to characterize several CNT: epoxy composite systems. This characterization approach was applied to composite systems with (1, 4 and 5) CNT weight percentages. Additionally, imaging XPS results will be presented to provide further insight into the dispersion quality on the micron scale. Challenges associated with overlapping spectral features, charging and a variety of other considerations regarding the surface and the bulk of the sample will be discussed.

6:00pm **AS+BI+MC-WeA12 Measuring Schmutz: Accounting for Adventitious Carbon Contamination in X-ray Absorption Spectra of Carbon-Based Materials***, **Filippo Mangolini**, J.B. McClimon, J. Hilbert, R.W. Carpick*, University of Pennsylvania

Near-edge X-ray absorption fine structure (NEXAFS) spectroscopy is one of the most powerful weapons in the surface-analysis arsenal, since it provides insights into the local ordering, bonding configuration, oxidation state, and hybridization of the elements present in the near-surface region (information depth: ~5 nm). NEXAFS analyses are commonly performed under the assumption of chemical and structural homogeneity within the nanometer-depth scale probed. Unfortunately, this does not hold for the vast majority of solid surfaces due to the presence of complex surface and near-surface structures (*e.g.*, natural oxides, contamination) and can lead to large errors when analyzing elements that are simultaneously present in multiple layers. This is particularly challenging for carbon-containing materials previously exposed to air, as their carbon K-edge NEXAFS spectra are a convolution of the spectrum of the material under investigation and that of the adventitious carbon contamination. While analysis methods for determining the composition and thickness of each layer in a multilayer system without applying any destructive technique have been developed for X-ray photoelectron spectroscopy, no corresponding methodology has ever been reported for NEXAFS spectroscopy.

Here, we present a novel, non-destructive, and generally-applicable method for accounting for the contribution of thin overlayers (with thickness smaller than the information depth) from NEXAFS spectra of two-layered systems (constituted by a substrate covered by a surface layer) to give the corrected NEXAFS spectrum of the substrate. The new methodology is applied to NEXAFS data acquired on air-exposed hard carbon-based materials (ultrananocrystalline diamond and hydrogenated amorphous carbon) and allowed for the removal of the contribution of adventitious carbon contamination from the as-acquired spectra to give the intrinsic photo-absorption NEXAFS spectra of the materials under investigation. The results demonstrated that, in the case of amorphous carbon-based materials, significant errors, between 5% and 20%, could be introduced in the computation of the fraction of carbon atoms in different hybridization states if the contribution from the carbonaceous contamination layer is not removed from the as-acquired NEXAFS spectra. We also extract information about the composition and bonding found in the contamination layer.

The development of this novel methodology has important implications for the thorough investigation of the near-surface region of carbon materials as well as of the phenomena occurring in them in response to different energetic inputs (*e.g.*, temperature, mechanical stress).

In-Situ Spectroscopy and Microscopy Focus Topic
Room: 313 - Session IS+2D+MC+NS+SP+SS-WeA

In-Situ Scanning Microscopy
Moderator: Markus Ammann, Paul Scherrer Institut

2:20pm **IS+2D+MC+NS+SP+SS-WeA1 *In Situ* Studies of Model Fuel Cells***, **Zhi Liu***, Lawrence Berkeley National Laboratory **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields. Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will give an overview of science projects at ALS BL9.3.2 in heterogeneous catalysis and electro-chemistry using these new systems. Furthermore, I will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell at ALS BL9.3.1. We believe the successful development of soft and hard X-ray APXPS endstations will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

3:00pm **IS+2D+MC+NS+SP+SS-WeA3 Probing of Nanoscale Objects in Reactive Liquids through Membranes using Near-Field Microwave Microscopy***, **Alexander Tselev**,* Oak Ridge National Laboratory*, A. Komakov*, National Institute of Standards and Technology (NIST)

Many functional objects (and interfaces) have to be studied in situ when the object is immersed in liquid environment. In addition, for energy, chemical, (bio-) medical and other applications, there is a need to study the encapsulated objects, which otherwise can be chemically reactive or toxic. These samples are often mesoscopically small or exist in minuscule quantities. Recently, we have developed a process for preparation of liquid-filled cells sealed with ultrathin membranes. Such cells can be implemented for in-situ studies using, for example, electronor soft x-ray microscopy due to a high transparency of these membranes to electron beams. However, in many cases electron microscopy is an invasive technique due to various electron beam induced parasitic effects (e.g. radiolysis or beam induced deposition). To overcome these impediments, we demonstrate the scanning microwave impedance microscopy (sMIM) to image different nanoscale objects immersed in the liquid environment through 30 nm SiN membranes. In the sMIM, microwaves of a frequency of 3 GHz are sent through a coaxial cable connected to a shielded cantilever probe fully compatible with an AMF microscope. The sharp probe tip provides “focusing effect” for the electric component of the microwave. For imaging, the tip is brought into gentle mechanical contact with a membrane. Amplitude and phase of microwaves reflected from the probe are monitored. Since the wave reflection is dependent on the tip-sample system impedance, reflected waves carry information about sample local properties. The effective distance into the sample depth, where the tip-induced field enhancement takes place, is approximately equal to the tip apex radius. Since the membrane thickness is smaller compared to the tip radius of a typical probe (about 50 nm for a fresh tip), the tip-sample impedance is dependent on the

dielectric properties of the material beneath membrane, and therefore, it is possible to "see" through the membrane. We demonstrate imaging of different combinations of model liquids and nanoparticles: water and water-based solutions (ε~80), organic solvents (ε~10-25), and oils (ε~2-3) containing Ni metal, polystyrene (ε~2.5) and PbO (ε~25) particles. This technique can be further implemented for a broad range of objects in confined liquids, and can be used to monitor interfacial electrochemical reactions. Imaging with sMIM was performed at CNMS, which is sponsored at ORNL by the SUFD, BES, US DOE.

4:20pm **IS+2D+MC+NS+SP+SS-WeA7 Caught in the Act! Live Observations of Catalysts Using High-Pressure Scanning Probe Microscopy**, ***Irene Groot***, Huygens-Kamerlingh Onnes Laboratory, Leiden University, Netherlands **INVITED**

Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra) high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra) high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts *in situ* under industrially relevant conditions.

This talk focuses on the development of scanning probe microscopy for *operando* observations of active model catalysts. In our group, we have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. As a proof of principle, results for the fruit fly of surface science, *i.e.* CO oxidation, will be shown. But additionally, results for more complex reactions such as NO reduction, Fischer-Tropsch synthesis, desulphurization, and production of chlorine will be discussed.

5:00pm **IS+2D+MC+NS+SP+SS-WeA9 X-ray Photoelectron Spectroscopy Studies of H_2O Dissociation on Pre-oxidized Al (111) and Cu (111) Single Crystal Surface**, ***Qianqian Liu***, SUNY, Binghamton University, *X. Tong*, Brookhaven National Laboratory, *G.W. Zhou*, SUNY, Binghamton University

Dissociation of H_2O molecules on ultrathin oxide overlayers formed on metal surfaces plays a critical role in many catalytic reactions. However, the effects of chemical states and thickness of oxide overlayers on the microscopic process of H_2O dissociation are still poorly understood. In this work, X-ray photoelectron spectroscopy (XPS) is employed to study H_2O dissociation on oxidized Al (111) and Cu (111) surfaces with controlled chemical states and thicknesses of the oxide films. For Al (111), the experiment was performed under two water vapor pressures (10^{-6} Torr and 5 Torr) on aluminum oxide films with the thicknesses varying from 2.47 Å to 5.14 Å; for Cu (111), the experiment was performed by varying the water vapor pressure from 10^{-7} Torr to 10^{-5} Torr and temperature from 100°C to 450°C on the oxide film with a constant thickness. Al (2p), Cu (2p), Cu (LMM) and O (1s) spectra were monitored by XPS after each oxygen exposure followed by subsequent H_2O exposure. Upon exposing the oxide to water vapor, the O (1s) peak shifts to a higher energy and becomes broader. A detailed analysis of the spectra indicates that H_2O molecules dissociate into OH groups for both oxidized Al and Cu surfaces. However, the subsequent reaction of OH groups with the oxide films on Cu (111) and Al (111) surfaces are dramatically different. On the oxidized Al(111) surface, OH is further incorporated into the aluminum oxide that results in the thickening of the oxide film, whereas on the oxidized Cu (111) surface, OH works as a reducing agent to remove oxygen from the oxide film that results in the thinning of the Cu oxide film. The microscopic processes underlying the differences in H_2O dissociation on oxidized Al (111) and Cu (111) will be described in detail.

5:20pm **IS+2D+MC+NS+SP+SS-WeA10 Operando APXPS of the Liquid-Solid Interface: Au Oxidation**, ***Ethan Crumlin***, *S.A. Axnanda, P.N.R. Ross, Z.L. Liu*, Lawrence Berkeley National Laboratory

Interfaces play an important role for many reaction processes and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to lithium ion batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. Previous capabilities of ambient pressure X-ray Photoelectron Spectroscopy (APXPS) have primarily only been able to observe the gas-solid and gas-liquid interfaces. However, recent enhancements now enable new APXPS systems to work at pressures larger then 20 Torr, and utilize 'Tender' X-rays (2.5 – 7 keV). These features provide new capabilities and opportunities for probing the liquid-solid and solid-solid interfaces. Using synchrotron X-rays at Lawrence Berkeley National Laboratory, the Advanced Light Source and our 'Tender' X-ray APXPS endstation that is outfitted with various *in situ/operando* features such as electrical leads to apply electrical potentials and operates at pressures >20 Torr, to observe the liquid-solid interface of a gold foil electrode that has been immersed and partially removed from a liquid electrolyte. This talk will provide details on how we used this technique to probe liquid-solid interface and in real-time observe the oxidation of the gold foil electrode under varying applied potentials and different electrolyte solutions.

5:40pm **IS+2D+MC+NS+SP+SS-WeA11 Water on ZnO(10-10) Investigated by Ambient Pressure X-ray Photoelectron Spectroscopy**, ***Chris Goodwin***, University of Delaware, *A. Boscoboinik*, Brookhaven National Lab, *C. Arble, J.T. Newberg*, University of Delaware

The extent to which ZnO hydroxylates under ambient conditions can significantly influence catalytic properties. Thus, it is critical to understand the composition of different ZnO terminations as a function of relative humidity (RH) in order to elucidate the true interfacial surface terminations. In this talk we present results of ambient pressure XPS (APXPS) for water exposures to a ZnO(10-10) single crystal. It will be shown that ZnO(10-10) extensively hydroxylates at the interface, and both molecular and dissociative water increase as the RH increases. These results are consistent with simulations in the literature that highlight the efficacy for ZnO(10-10) to dissociate water.

Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+MC+NS+SS-ThM

APT Analysis of Semiconductors, Magnetic and Oxide Materials
Moderator: Paul Bagot, Oxford University, UK, Daniel Perea, Pacific Northwest National Laboratory

8:00am **AP+AS+MC+NS+SS-ThM1 A Vision for Atom Probe Tomography**, ***Thomas F. Kelly***, CAMECA Instruments Inc **INVITED**

Atom Probe Tomography has undergone revolutionary changes in the past two decades. It is tempting to think that these changes are likely to be followed by a period of adjustment and maturation but not continued innovation. However, there are still many active opportunities for development of atom probe tomography. Some of these new technologies are already upon us. There are recent major developments in data reconstruction, detector technology, data mining, and correlative microscopy. Furthermore, application areas are evolving at a rapid pace. The equipment needed to serve some applications will necessarily be developing alongside the more fundamental operating components of atom probes.

This talk with review some recent developments that are just emerging and will offer a vision for where the field is headed. Some of the unproven concepts needed to reach this vision will be highlighted.

8:40am **AP+AS+MC+NS+SS-ThM3 Interfaces in Semiconductors: Application to Photovoltaic Materials**, ***Oana Cojocaru-Mirédin***, Max Planck Institut fur Eisenforschung GmbH, Germany, *R. Würz,* Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg, Germany, *D. Raabe*, Max Planck Institut fur Eisenforschung GmbH, Germany **INVITED**

$Cu(In,Ga)Se_2$ (CIGS), $Cu_2ZnSnSe_4$ (CZTSe), and multicrystalline Si (mc-Si) solar cells possess a high efficiency [1], despite the polycrystalline structure of the absorber layer. One of the major factors controlling the cell efficiency is the diffusion of the impurities during the fabrication process into the absorber layer and to the p-n junction [2]. However, the interaction between the defects and the impurities at the internal interfaces is not completely understood. This is due to a lack of information on the local chemical changes across the internal interfaces at the nanoscale.

As a step towards a better understanding of the impurity redistribution at the internal interfaces, we have developed novel approaches of preparing site-specific atom probe specimens using combined focused ion beam (FIB), (scanning) transmission electron microscopy ((S)TEM) and electron backscattered diffraction (EBSD). These approaches allow selected GBs in polycrystalline CIGS, CZTSe and mc-Si layers to be studied by atom probe tomography (APT).

Several examples of correlative EBSD-TEM-APT (see Figure 1) and STEM-APT (see Figure 2) studies will be presented in this work. Using APT, segregation of impurities at the GBs was directly observed. APT data of various types of GBs will be presented and discussed with respect to the possible effects on the cell efficiency.

[1] Empa [Internet]. Empa.ch: A new world record for solar cell efficiency, 2013. Available from: http://www.empa.ch/plugin/template/empa/3/131438/---/l=2 [cited 2013 January 18].

[2] J. L. Shay, S. Wagner, H. M. Kasper, Appl. Phys. Lett. 27 (1975) 89, S. Yip and I. Shih, Proceedings of the 1st World Conference on Photovoltaic Energy Conversion (IEEE, Piscataway, 1994), p.210.

9:20am **AP+AS+MC+NS+SS-ThM5 Analysis of Discontinuous InGaN Quantum Wells by Correlated Atom Probe Tomography, Micro-Photoluminescence, and X-ray Diffraction**, *J. Riley, X. Ren,* Northwestern University, *D. Koleske,* Sandia National Laboratories, ***Lincoln Lauhon***, Northwestern University

In(x)Ga(1-x)N quantum wells are the foundation of solid-state lighting, with excellent quantum efficiencies despite high densities of defects. While there is as yet no universally accepted explanation for the high-efficiency, it is clear that carrier localization plays a role. Consistent with this picture, the quantum efficiencies of some samples can be improved by annealing and hydrogen gas to produce discontinuous quantum wells. However, the standard analysis of quantum well widths and composition by high-resolution x-ray diffraction is complicated by such complex morphologies. Specifically, the influence of surface roughness, and interfacial diffuseness, and planar continuity may be difficult to deconcolve. We will describe correlated analysis of continuous and discontinuous InGaN quantum wells by atom probe tomography, micro-photoluminescence, high-resolution x-ray diffraction, and atomic force microscopy. We find that precise composition profiles extracted from atom probe analysis enable refinement of x-ray diffraction peak fitting in the case of continuous quantum wells, and a better estimate of indium mole fraction and quantum well width. For discontinuous quantum wells, atom probe analysis enables simple models to be integrated into routine x-ray diffraction modeling to enable reliable extraction of indium mole fraction and better correlation with photoluminescence spectra. Correlation of atomic force microscopy tomographic images and micro-photoluminescence spectra over common sample areas, together with site-specific lift out techniques, will be presented to explore the surprising coexistence of high quantum efficiency and inhomogeneous broadening due to the complex underlying quantum well morphology.

9:40am **AP+AS+MC+NS+SS-ThM6 Atom Probe Tomography Characterization of Doped Epitaxial Oxide Multi-Layered Structures**, ***Nitesh Madaan***, *A. Devaraj, Z. Xu, M.I. Nandasiri, S.A. Thevuthasan*, Pacific Northwest National Laboratory

Atom probe tomography is the state of the art 3D microscopy technique with sub-nanometer scale spatial resolution and ppm level mass sensitivity. For complex heterogeneous materials the accurate artifact-free reconstruction of collected data is quite a challenging task due to varying local evaporation fields leading to non-hemispherical evolution in the tip shape during the APT analysis. In this work we utilized laser assisted APT to analyze alternate multilayer oxide thin film structure of Samaria doped ceria (SDC) and Scandia stabilized zirconia (ScSZ), grown epitaxially on sapphire substrate, which is potentially useful for solid oxide fuel cells due to their high ionic conductivity. By analyzing the sample in different orientations (top-down, side-ways, and back-side) and comparing with dynamic tip shape evolution using level set simulations for similar geometries, an attempt was made to understand and decouple the APT evaporation artifacts from the real physical sample features. This study would help provide insights to improve the APT reconstruction process for complex multi-layered thin film materials.

11:00am **AP+AS+MC+NS+SS-ThM10 Atom Probe Tomography and Field Evaporation of Insulators and Semiconductors: Theoretical Issues**, ***Hans Kreuzer***, Dalhousie University, Canada **INVITED**

After reviewing the physics and chemistry in high electrostatic fields and summarizing the theoretical results for Atom Probe Tomography of metallic tips, we turn to the new challenges associated with insulators and semiconductors with regard to local fields inside and on the surface of such materials. The recent (theoretical) discovery that in high fields the band gap in these materials is drastically reduced to the point where at the evaporation field strength it vanishes will be crucial in our discussion.

11:40am **AP+AS+MC+NS+SS-ThM12 Atom Probe Tomography Investigation of the Microstructure of Multistage Annealed Nanocrystalline $SmCo_2Fe_2B$ Alloy with Enhanced Magnetic Properties**, ***Xiujuan Jiang***, *A. Devaraj,* Pacific Northwest National Laboratory, *B. Balamurugan,* University of Nebraska-Lincoln, *J. Cui,* Pacific Northwest National Laboratory, *J. Shield*, University of Nebraska-Lincoln

Permanent magnets have garnered great research interest for energy applications. The microstructure and chemistry of a permanent magnet candidate—$SmCo_2Fe_2B$ melt-spun alloy—after multistage annealing was investigated using high resolution transmission electron microscopy (HRTEM) and atom probe tomography. The multistage annealing resulted in an increase in both the coercivity and magnetization as is desired for permanent magnets design. The presence of $Sm(Co,Fe)_4B$ (1:4:1) and $Sm_2(Co,Fe)_{17}B_x$ (2:17:x) magnetic phases were confirmed using both techniques. Fe_2B at a scale of ~ 5 nm was found by HRTEM precipitating within the 1:4:1 phase after the second-stage annealing. Ordering within the 2:17:x phase was directly identified both by the presence of antiphase boundaries observed by TEM and the interconnected isocomposition surface network found in 3D atom probe results in addition to radial distribution function analysis. These observed variations in the local chemistry after the secondary annealing were considered pivotal in improving the magnetic properties.

12:00pm **AP+AS+MC+NS+SS-ThM13 Detector Dead-time Effects on the Accurate Measurement of Boron in Atom Probe Tomography**, ***Frederick Meisenkothen***, National Institute of Standards and Technology (NIST), *T.J. Prosa,* CAMECA Instruments Inc., *E.B. Steel,* NIST, *R.P. Kolli*, University of Maryland, College Park

The atom probe tomography (APT) instrument uses a time-of-flight (TOF) mass spectrometer to identify ions that are field ionized and evaporated from the apex of a needle-like nano-tip specimen. A pulse event, either laser or voltage, is used to trigger field evaporation and to initiate the timing sequence for the mass spectrometer. Ideally, a single atom is field evaporated during a single pulse event. However, it is also common to have multi-hit detection events where more than one ion strikes the detector between pulses. For reasons not completely understood, some elements, such as boron, are prone to field evaporate in multi-hit detection events when compared to other elements, and a large fraction of the boron signal is reportedly lost during acquisition. Obtaining an improved understanding of the field evaporation behavior of boron at different concentration levels, in view of the limited ability of the detection system to resolve multi-hit detection events, may lead to new ways to compensate for the boron signal loss.

A nominally pure boron sample was chosen as a high boron concentration material while the boron implanted silicon, NIST-SRM2137, (1E15 atoms cm^{-2} retained dose) was chosen as the low boron concentration material. A dual-beam FIB/SEM instrument, with an *insitu* lift-out system, was used to prepare the APT specimen tips from the bulk materials. A laser pulsed LEAP 4000X Si* instrument was used to acquire APT data sets for each of the specimen tips. Custom software scripts were used to filter the data sets and extract the ion information associated with specific search criteria, e.g. event multiplicity, which is the number of ions within a given multi-hit event. Ion correlation analysis was used to graphically demonstrate the detector dead-time effect. In the present work, more than 60% of the detected boron signal resided within the multi-hit detection events, for both the high and low boron concentration samples.

* Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

Helium Ion Microscopy Focus Topic
Room: 316 - Session HI+2D+AS+BI+MC-ThM

Fundamental Aspects and Imaging with the Ion Microscope

Moderator: Gregor Hlawacek, Helmholtz-Zentrum Dresden - Rossendorf, Stuart Boden, University of Southampton

8:00am **HI+2D+AS+BI+MC-ThM1 He+ and Ne+ Ion Beam Microscopy and Microanalysis**, ***David C. Joy***, University of Tennessee, Oak Ridge National Laboratory **INVITED**

After one hundred years of use the electron microscope is now being overtaken by ion beam systems because of their many advantages. A wide variety of different ions are available, each of which has its own particular strengths, but the two most commonly used at present are Helium (He+) and Neon (Ne+). Changing from one to the other takes only a couple of minutes to complete. for operation at beam energies between 20 and 50kV both He+ and Ne+ generate 'ion induced secondary electrons' (iSE) which yield images which are comparable with those from a conventional SEM but offer image resolutions of 0.4nm or less even on bulk samples, a much greater depth of field, and an enhanced signal to noise ratio. At typical imaging currents between 10-12 to 10-14Amps damage to most samples is very limited for He+ although more severe for Ne+ but at higher beam currents both He+ and Ne+ can pattern, deposit, or remove, a wide range of materials. In such applications He+ provides the best resolution, but Ne+ is much faster.

The production of X-rays depends on the speed of the incident particle, not on its energy. At typical operating energies the He+ or Ne+ ions are traveling too slowly to generate X-rays so another approach is required for chemical microanalysis. The most promising option is "Time of Flight-Secondary Ion Mass Spectrometry" (TOF-SIMS). Here the incoming ion "splashes" material from the top few layers of the specimen surface. These fragments are then characterized by determining their mass to charge ratios. The chemical data this generates is much more detailed than the bare list of elements that is produced by X-ray microanalysis.

8:40am **HI+2D+AS+BI+MC-ThM3 Gas Field Ion Sources**, ***Jason Pitters***, *R. Urban,* National Institute for Nanotechnology, Canada, *R. Wolkow*, University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

Single atom tips (SATs) prepared by the spatially controlled field assisted etching method are proving to have utility as ion sources, electron sources and in scan probe applications.

As Gas Field Ion Sources (GFISs), there is potential for operation in scanning ion microscopes (SIMs) and our efforts to prepare and characterize SAT ion emission will be discussed. It will be shown that etching to a single atom tip occurs through a symmetric structure and leads to a predictable last atom. SATs can be prepared reproducibly with emission along a fixed direction for all tip rebuilds. It will also be shown that the emission properties of the SAT can be altered by shaping of the tip shank during the etching procedure. In this manner, the operating voltage can be controlled and a lensing effect of the tip base is demonstrated. During formation, the tip shape can be evaluated by using both helium and neon imaging gases. The stability of helium and neon ion beams generated by SATs will also be demonstrated and compared to other tip orientations. The remarkable robustness of these tips to atmosphere exposure will also be shown and the ability to prepare SATs from material other than tungsten will be demonstrated.

SATs also have utility in electron emission. By shaping the tip appropriately, electron emission characteristics can also be tailored and the coherence properties of an SAT will be presented as deduced from holographic measurements in a low-energy electron point source microscope. Initial utility in scan probe experiments including atomic force microscopy and scanning tunneling microscopy will also be discussed.

9:20am **HI+2D+AS+BI+MC-ThM5 Ion Beam Profiles Generated by W(111) Single Atom Tips**, ***Radovan Urban***, *R. Wolkow,* University of Alberta and The National Institute for Nanotechnology, Canada, *J.L. Pitters*, National Institute for Nanotechnology, Canada

Single atom tips (SATs) gained significant attention over the past decade because they serve as high brightness, field emission electron sources and gas field ion sources (GFISs). Small virtual source size makes these attractive candidates for advanced scanning imaging applications such as SEM, TEM, and scanning ion microscopy (SIM) as well as for non-staining ion beam writing applications.

The ion beam diameter σ, together with total ion current I generated by a single surface atom of W(111) nanotip, are crucial parameters which determine angular current density and brightness of gas field ion sources. It is, therefore, essential to understand underlying mechanisms that govern beam width. Furthermore, mapping both σ and I to a large parameter space of tip temperature, imaging gas pressure, and extraction voltage is necessary to optimize gas field ion source operation. In this contributions we will explore both σ and I as a function of temperature and extraction voltage at different imaging gas pressures using a field ion microscope (FIM) to monitor beam shape and total current. The qualitative model of our results will be also discussed. Finding "the best imaging voltage" for a SAT will be briefly discussed.

9:40am **HI+2D+AS+BI+MC-ThM6 Defect Observation by using Scanning Helium Ion Microscopy**, ***Hongxuan Guo***, *L. Zhang, D. Fujita*, National Institute for Materials Science (NIMS), Japan

Scanning helium ion microscopy (HIM) is an innovative method to characterize surface of various materials. With a secondary electron detector (SED) and a micro plate detector (CPD), Orion Plus system can obtain surface information including morphology , composition, and crystal orientation. [1, 2] Improve the abilities of characterization of materials with HIM will benefit the develop of new materials, such as structure materials including metals, ceramics and others.

In this presentation, we will show the investigation of the crystal structure of metal with HIM. We prepared an sample stage with a reflector that can be used to obtain the transmission helium ions intensities in the samples. With this sample stage, we observed the Ni-Co base super alloy and aerogel composed with hollow nanosphere. The Rutherford backscattered image (RBI) of metal surface show different orientation of poly crystal. The nano-twins and other defects in Ni-Co base superalloy were investigated by HIM in scanning and transmission mode. The nano-twins also be observed by other techniques, such as transmission electron microscopy and electron backscatter diffraction. The scattering of helium ions with different energy was analyzed. This work provide some new methods to improve the research on defects and structure of crystal.

[1]. H. X. Guo, D. Fujita, Scanning helium ion microscopy, Characterization of Materials, 2nd Edition(Wiley, New York, 2012)

[2]. H. X. Guo. J. H. Gao, M. S. Xu, D. Fujita, Applied Physics Letters, 104, 031607 , 2014

11:00am **HI+2D+AS+BI+MC-ThM10 Helium Ion Microscopy (HIM) for the Imaging of Biological Samples at Sub-nanometer Resolution**, ***James Fitzpatrick***, Salk Institute for Biological Studies **INVITED**

Scanning Electron Microscopy (SEM) has long been the standard in imaging the sub-micrometer surface ultrastructure of both hard and soft materials. In the case of biological samples, it has provided great insights into their physical architecture. However, three of the fundamental challenges in the SEM imaging of soft materials are that of limited imaging resolution at high magnification, charging caused by the insulating properties of most biological samples and the loss of subtle surface features by heavy metal coating. These challenges have recently been overcome with the development of the Helium Ion Microscope (HIM), which boasts advances in charge reduction, minimized sample damage, high surface contrast without the need for metal coating, increased depth of field, and 5 angstrom imaging resolution. We demonstrate the advantages of HIM for imaging biological surfaces as well as compare and contrast the effects of sample preparation techniques and their consequences on sub-nanometer ultrastructure.

11:40am **HI+2D+AS+BI+MC-ThM12 Helium Ion Microscopy of Biological Cells**, ***Natalie Frese***, *A. Beyer, M. Schürmann, B. Kaltschmidt, C. Kaltschmidt, A. Gölzhäuser*, University of Bielefeld, Germany

In this presentation HIM images of biological cells are presented. The presented study focuses on neuronal differentiated human inferior turbinate stem cells, mouse neurons and mouse fibroblasts. The cells were prepared by critical point drying or freeze drying and a flood gun was used to compensate charging, so no conductive coating was necessary.

Therewith, extremely small features at native cell surfaces were imaged with an estimated edge resolution of 1.5 nm. Due to the size of the structures and the preparation methods of the cells the observed features could be an indicator for lipid rafts. This hypothesis will be discussed.

12:00pm **HI+2D+AS+BI+MC-ThM13 Helium Ion Microscopy Analysis of Ag Nanoparticle Implanted Biological Samples for MILDI-MS (Matrix Implanted Laser Desorption/Ionization) Imaging**, *S. Shubeita,* Rutgers University*, L. Muller,* NIDA-IRP*, H.D. Lee, C. Xu,* Rutgers University*, D. Barbacci,* Ionwerks Inc.*, K. Baldwin,* NIDA-IRP*, J.A. Schultz,* Ionwerks Inc.*, L. Wielunski,* ***Torgny Gustafsson****, L.C. Feldman,* Rutgers University*, A.S. Woods*, NIDA-IRP

MILDI mass spectrometry is an emerging tool for detecting changes in brain tissue. An ~20 nm thick region of rat brain tissue implanted with $10^{13}/cm^2$ $Au_{(400)}^{4+}$ nanoparticle (NP) ions at 40 keV, produces analytically useful signals of lipids, peptides and proteins using a pulsed nitrogen laser [1]. When a dose of $10^{12}/cm^2$ 500 eV AgNP (approximately 6 nm diameter) is implanted as a matrix, only lipids are detected [2]. To understand this it is essential to measure the spatial distribution of the nanoparticles. We have used Rutherford Backscattering and Helium Ion Microscopy imaging to determine the Ag NP distributions and areal densities in an implanted coronal rat brain section. We then correlate the ion beam analysis and imaging with individual lipid intensities from several hundred MILDI mass distributions. The results show a high degree of uniformity of the Ag atomic and particulate distribution on a sub-micron scale among different regions of the tissue. Helium Ion Microscopy provides verification of NP matrix uniformity, validating the use of MILDI for quantitative mass analysis.

This work is partially supported by NSF (DMR 1126468), NIH (R44DA030853-03) and IAMDN.

[1] A. Novikov et al, *Analytical Chemistry* 76 (2004) 7288. [2] S. N. Jackson et al, *Analyt. and Bioanal. Chem.* (e-pubed Dec 2013).

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+2D+AS+EM+MC+NS+SS-ThM

Probing Electronic and Transport Properties
Moderator: An-Ping Li, ORNL, Corentin Durand, ORNL

8:00am **SP+2D+AS+EM+MC+NS+SS-ThM1 Investigation of the Electronic and Structural Properties of Metal Free Naphthalocyanine Vapor Deposited on Au(111)**, ***Bryan Wiggins***, University of Chicago, *K.W. Hipps*, Washington State University

Naphthalocyanines (Ncs) are promising candidates for future components in electronic devices and applications. To maximize the efficiency of Nc devices, it is critical to understand their structural and electronic properties and how these are impacted by deposition methods. The formation of a metal free naphthalocyanine (H_2Nc) self-assembled monolayer on a Au(111) crystal was investigated by scanning tunneling microscopy under ultra-high-vacuum conditions at room temperature. A rigorous purification and processing procedure was developed to produce high purity, low defect, and well-ordered monolayers. High-resolution STM images reveal epitaxial growth of H_2Nc on Au(111) with the observed structure having a molecular spacing of 1.6 ± 0.05 nm, with molecules orientated slightly off (roughly 2.5°) the low density packing direction of Au(111). A commensurate structure having 4 molecules per unit cell and unit cell parameters of A = 3.25 ± 0.05 nm, B = 3.17 ± 0.05 nm, and α = 87.5 ± 2° is proposed. Orbital-mediated tunneling spectroscopy was used to examine the electronic properties of individual molecules within the thin film. The first ionization potential and electron affinity of H_2Nc adsorbed on Au(111) were measured to be −0.68 ± 0.03 and 1.12 ± 0.02 eV, relative to the Fermi energy.

8:20am **SP+2D+AS+EM+MC+NS+SS-ThM2 The Fundamentals of Charge Transport at Oxide and Ferroelectric Interfaces**, ***Ramsey Kraya***, *L.Y. Kraya*, University of Pennsylvania

Here we investigate how charge transport properties at metal-semiconductor interfaces scale down to the nanoscale regime, comparing the properties to macroscopic interfaces and providing a perspective on what it means to device manufacturing. Strontium titanate - the prototypical oxide material - has been widely studied for applications in thermoelectrics, nanoelectronics, catalysis, and other uses, and behaves as an n-type semiconductor when doped. We investigated how charge transport is effected at interfaces to stronitium titanate under a wide range of conditions - by varying contact size, interface shape, dopant concentration, and surface structure and in various combinations. The results of the analysis have wide ranging implications, especially for ferroelectric oxide materials and serves as the basis for understanding and controlling switching effects - both polarization and oxygen migration based switching.

8:40am **SP+2D+AS+EM+MC+NS+SS-ThM3 Epitaxial Graphene on Nanostructured Silicon Carbide**, ***Phillip First***, Georgia Institute of Technology **INVITED**

Graphene grown epitaxially on silicon carbide conforms to nanofacetted step edges, even for step heights of many nanometers. The "sidewall" nanoribbons that result show astounding transport characteristics (~15 um ballistic length at room temperature), as demonstrated by others,[1] but the physical basis for these results is still not certain. In our STM measurements of sidewall nanoribbons, we find an extended 1D region with electronic structure much different than 2D graphene. Spectroscopic results on graphene near nanofacet corners indicate a strain gradient and a rapid change in the doping. Such strong gradients may be key to understanding the ballistic transport in this system. P

[1]J. Baringhaus, M. Ruan, F. Edler, A. Tejeda, M. Sicot, AminaTaleb-Ibrahimi, A.-P. Li, Z. Jiang, E. H. Conrad, C. Berger, C. Tegenkamp and W. A. de Heer, "Exceptional ballistic transport in epitaxial graphene nanoribbons," *Nature,* **506,** 349 (2014).

9:20am **SP+2D+AS+EM+MC+NS+SS-ThM5 Conductivity of Si(111) - 7 × 7: The Role of a Single Atomic Step**, *B. Martins,* University of Alberta and The National Institute for Nanotechnology, Canada*, M. Smeu, H. Guo,* McGill University, Canada*,* ***Robert Wolkow***, University of Alberta and The National Institute for Nanotechnology, Canada

The Si(111) - 7 × 7 surface is one of the most interesting semiconductor surfaces because of its

complex reconstruction and fascinating electronic properties. While it is known that the Si - 7 × 7 is

a conducting surface, the exact surface conductivity has eluded consensus for decades as measured

values differ by 7 orders of magnitude. Here we report a combined STM and transport measurement

with ultra-high spatial resolution and minimal interaction with the sample, and quantitatively determine the intrinsic conductivity of the Si - 7 × 7 surface. This is made possible by the capability of

measuring transport properties with or without a single atomic step between the measuring probes:

we found that even a single step can reduce the surface conductivity by two orders of magnitude.

Our first principles quantum transport calculations confirm and lend insight to the experimental

observation.

9:40am **SP+2D+AS+EM+MC+NS+SS-ThM6 Asymmetric Electron Transport Revealed at Monolayer-Bilayer Graphene Junctions by Atomic-Scale Scanning Tunneling Potentiometry**, *K. Clark, X. Zhang, J. Park,* Oak Ridge National Laboratory*, G. Gu,* University of Tennessee*, G. He, R.M. Feenstra,* Carnegie Mellon University*, **An-Ping Li***, Oak Ridge National Laboratory

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films [1]. These heterojunctions provide us fascinating playground for exploring electronic and transport properties in 2D materials. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries, changes in layer thickness, and substrate steps, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a major impact on the electronic properties, especially the transport, in 2D materials.

Here, we present our recent study on an asymmetric electron transport upon bias polarity reversal at individual monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC (0001), revealed by multi-probe scanning tunneling potentiometry [2,3]. A greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, and the difference remains nearly unchanged when bias exceeds a threshold. A thermovoltage is measured across the boundary due to the thermopower difference between the two sides, which however is too small to account for the observed asymmetry. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Our theoretical analysis finds that Friedel charge oscillation opens a gap for electrons with wave vectors perpendicular to the boundary. The Friedel gaps are different on the monolayer and bilayer sides, which can shift under bias and lead to asymmetric transport upon reversing the bias polarity. A quantitative agreement is seen between experiment and theory on both the sign and the magnitude of the asymmetry.

1 "Heteroepitaxial Growth of Two-Dimensional Hexagonal Boron Nitride Templated by Graphene Edges", L. Liu, J. Park, D. A. Siegel, K. F. McCarty, K. W. Clark, W. Deng, L. Basile, J.-C. Idrobo, A.-P. Li, G. Gu, *Science***343**, 163-167 (2014).

2 "Spatially Resolved Mapping of Electrical Conductance around Individual Domain (Grain) Boundaries in Graphene", K. W. Clark, X.-G. Zhang, I. V. Vlassiouk, G. He, R. M. Feenstra, and A.-P. Li, *ACS Nano*. **7** (9), 7956-7966 (2013).

3 "Friedel Oscilation-Induced Energy Gap Manifested as Transport Asymmetric at Monolayer-Bilayer Graphene Boundaries", K. W. Clark, X.-G. Zhang, G. Gu, G. He, R. M. Feenstra, and A.-P. Li, *arXiv:* 1401.1796, *Physical Review X***4** (1), 011021 (2014).

11:00am **SP+2D+AS+EM+MC+NS+SS-ThM10 Defect-mediated Transport in CVD-grown Monolayer MoS_2**, ***Corentin Durand****, J. Fowlkes,* Oak Ridge National Laboratory*, S. Najmaei, J. Lou,* Rice University*, A.P. Li*, Oak Ridge National Laboratory

Transition metal dichalcogenides like molybdenum disulphide (MoS_2) have attracted great interest as candidate to fill the need of 2 dimensional semiconductor materials. By controlling the thickness, the bandgap of MoS_2 thin films can be tuned from 1.2 eV (bulk material, indirect bandgap) to 1.8 eV (monolayer film, direct bandgap). Recently, researchers succeeded in growing monolayered MoS_2 by chemical vapor deposition (CVD) on silicon dioxide (SiO_2) substrate, showing the possibility of low cost scalable device fabrication. However, the mobility reported on exfoliated MoS_2 monolayers exceeds 200 $cm^2.V^{-1}.s^{-1}$, whereas the measurements realized on CVD growth MoS_2 monolayers reveal a mobility value that is usually 1-2 orders of magnitude lower. Here, we study the transport properties of CVD-grown monolayer on SiO_2/Si substrate. We directly measure the resistivity and the mobility of the material with a field-effect transistor architecture by using a cryogenic four-probe scanning tunneling microscope (STM), the Si substrate being used as back-gate. In order to ensure reliable electrical contacts, we fabricate platinum pads (4x4 μm^2) on individual MoS_2 crystal domains by using an electron-beam induced deposition technique. The combination of the STM scanners and a scanning electron microscope (SEM) enables us to connect the STM tips on those pads and thereby establish the contacts on this material without any subsequent lithography process, avoiding contaminations introduced by other technological steps. An electron hopping process in localized charge trapping states appears to dominate the transport behavior. We performed temperature-dependent measurements in the range of 82 K to 315 K which demonstrate a variable range hopping (VRH) transport with a very low mobility. Furthermore, the effects of electronic irradiation are examined by exposing the film to electron beam in the SEM in an ultra-high vacuum environment. We found that the irradiation process affect the mobility and also the carrier concentration of the material, with conductance showing a peculiar time-dependent relaxation behavior. It is suggested that the presence of defects such as vacancies and antisites create charge trapping states, leading to the low mobility. This is consistent with recent density functional theory calculations where these defects are shown to create localized gap states that can act as scattering centers and thereby reduce the mobility.

11:20am **SP+2D+AS+EM+MC+NS+SS-ThM11 Coherent One Dimensional Boundaries in Graphene and Hexagonal Boron Nitride Heterostructures**, ***Jewook Park****,* Oak Ridge National Laboratory*, L. Liu,* The University of Tennessee Knoxville*, D.A. Siegel, K.F. McCarty,* Sandia National Laboratories*, L. Basile, J.-C. Idrobo, K. Clark,* ORNL*, W. Deng,* The Univ. of Tennessee Knoxville*, C.P. Durand,* ORNL*, G. Gu,* The Univ. of Tennessee Knoxville*, A.P. Li*, ORNL

The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures where graphene and other atomic layer films such as monolayer hexagonal boron nitride (hBN) form phase-separated domains or both materials grow epitaxially onto a common crystalline substrate. By implementing the concept of epitaxy to 2D space, we developed and applied a new growth technique to hybrid isostructural but electrically dissimilar materials, such as the 2D epitaxial growth of hBN templated by graphene edge [1]. Scanning tunneling microscopy and spectroscopy measurements revealed a single-atomic-layer, in-plane heterostructure between graphene and hBN, as well as an abrupt 1D zigzag oriented boundary. In addition, the dI/dV conductance map unveiled the 1D interfacial states that are extended along, but localized at the boundary. We investigated spatial and energetic distributions of 1D boundary states. Also, low-energy electron microscopy and micro low-energy electron diffraction confirmed the heterostructure at mesoscopic scale and established that the graphene edge solely determines the crystallography of the hBN regardless of underlying the Cu(100) lattice. The Z-contrast scanning transmission electron microscopy further indicates an atomically sharp interface with a transition width of ~0.5 nm. We suggest that the graphene-hBN epitaxial heterostructure provides an excellent platform to explore heteroepitaxy in 2D space, and the unique functionalities at the 1D interface. [1] Lei Liu *et al*. *Science***343** 163 (2014)

11:40am **SP+2D+AS+EM+MC+NS+SS-ThM12 Charge and Spin Density Waves in Quasi One-Dimensional Atomic Wires**, ***Herbert Pfnür***, Leibniz Universität, Germany **INVITED**

Although free one-dimensional (1D) objects should exist only at T=0, atomic single wires or arrays embedded into a two- or three-dimensional environment exist even at room temperature and above, since they are stabilized by lateral interactions. These interactions not only stabilize, but also strongly modify the properties of the wires. Their 2D or 3D coupling, however, does not generally prevent observation of 1D properties with their complex variety of instabilities. Furthermore, these coupling can result in special 1D behavior not predicted by standard theories either in 1D or 2D. I will show several examples how atomic wires and wire arrays grown by self-assembly on semiconducting surfaces of Si and Ge acting as insulating substrates can be used to study in detail fundamental aspects of low-dimensional physics, such as charge density waves [1] and Luttinger liquid behavior [2], partially under explicit control of the atomic structure. Due to the low symmetry in these structures, large Rashba-type spin-orbit coupling is expected to lift the spin degeneracy of the metal-induced surface states. In this context new types of spin order were proposed , e.g. for Au/Si(553) [3] and found to be consistent with experiment. As a further example, the Pb/Si(557) system close to monolayer coverage turned out to be an intruiging model system that demonstrates the whealth of phenomena to be expected in quasi-1D physics. Adsorbate induced electronic stabilization leads to (223) refacetting of the (557) surface, to opening of a band gap, to Fermi nesting normal to the steps [4]., and to the formation of a charge density wave. Rashba splitting is so large that it causes in-plane anti-ferromagnetic spin polarization along the steps with twice the step periodicity resulting in a combined spin-charge density wave. New superstructures are formed by an excess Pb coverage up to 0.1ML due to ordered step decoration indicating strong electron-electron correlation across steps. This leads to new long range ordered states and formation of a sequence of 1D charge density waves up to a concentration of 1.5 ML, but also, as very recent angular and spin resolved photoemission studies show, to new ordered spin states.

[1] T. Tanikawa et.al. Phys. Rev. Lett. 93, 016801 (2004).

[2] C. Blumenstein et.al. Nat. Phys. 7, 776 (2011).

[3] S.C. Erwin, F. J. Himpsel, Nature Communications 1, 58 (2010); J. Aulbach et al. Phys. Rev. Lett. 111, 137203 (2013)

[4] C. Tegenkamp, D. Lükermann, H. Pfnür, B. Slomski, G. Landolt H. Dil, Phys. Rev. Lett. 109,

266401 (2012).

Spectroscopic Ellipsometry Focus Topic
Room: 304 - Session EL+AS+EM+MC+SS-ThA

Optical Characterization of Nanostructures and Metamaterials
Moderator: David Aspnes, North Carolina State University, Mathias Schubert, University of Nebraska-Lincoln

2:20pm **EL+AS+EM+MC+SS-ThA1 The Optical Properties of Metallic Nanostructures**, ***Bruno Gompf***, Universität Stuttgart, Germany **INVITED**

The entire optical response of a homogenous reciprocal sample can be characterized by eight basic physical properties: mean absorption, mean refraction, circular birefringence and circular dichroism, linear birefringence and linear dichroism (0°, 90°), linear birefringence and linear dichroism (-+45°). Always two out of the three main birefringence-dichroism pairs (basic anisotropies) are sufficient to jump from any point of the Poincare-sphere to any other. A common example is the Soleil-Babinet compensator. This implies that always two of the basic anisotropies generate artificial signals of the third [1]. Therefore even for perfect crystals it is hard to judge, what optical property lead to an observed polarization change.

In the case of inhomogeneous materials the permittivity additionally becomes k-dependent $\varepsilon_{ij}(\omega, k)$; it exhibits spatial dispersion. For most artificial nanostructures, dubbed metamaterials, the building blocks are in the range l/10 < P < l/2. During the last couple of years it has become clear that in general it is not possible for these kinds of materials to define *effective* optical parameters, which are independent of the angle of incidence of the probing light. There optical response is intrinsically k-dependent.

With Mueller-matrix spectroscopic ellipsometry the entire optical response of artificial nanostructures can be characterized. For this the Mueller-matrix elements $m_{ij}(\theta, \alpha, \omega)$, which depends on the angle of incidence q, the azimuth orientation a and the energy, had to be measured over the complete angular and a wide frequency range. Visualizing the results in polar contour plots enables a detailed analysis of how nanostructures influence the polarization state of light [2-4]. Most importantly, immediate experimental evidence is obtained for deviations from pure dielectric behaviour; i.e. the optical response cannot be explained by an effective $\varepsilon_{i,j}(\omega)$ alone but requires spatial dispersion.

In the talk the entire optical response of a some artificial nanostructures will be presented and some generalizations will be discussed, when spatial dispersion becomes important and how it can be distinguished from other optical properties leading to a mixing of polarization states, like birefringence and optical activity.

[1] J.Schellman and H.P.Jensen, Chem. Rev., 87, 1359 (1987.))

[2] B. Gompf, J. Braun, T. Weiss, H. Giessen, M. Dressel, U. Huebner, Phys.Rev.Lett. **106**,

185501 (2011).

[3] B.Gompf, B. Krausz, B. Frank, M. Dressel, Phys.Rev.B. **86**, 075462 (2012).

[4] A. Berrier, B. Gompf, Liwei Fu, T. Weiss, H. Schweizer, Phys.Rev.B. in print

3:00pm **EL+AS+EM+MC+SS-ThA3 Mueller Matrix Ellipsometry As a Powerful Tool for Nanoimprinted Grating Structure Metrology**, ***Xiuguo Chen***, *C.W. Zhang, S.Y. Liu*, Huazhong University of Science and Technology, China

Compared with conventional ellipsometric scatterometry, which only obtains two ellipsometric angles, Mueller matrix ellipsometry (MME, sometimes also referred to as Mueller matrix polarimetry) based scatterometry can provide up to 16 quantities of a 4 by 4 Mueller matrix in each measurement. Consequently, MME can acquire much more useful information about the sample and thereby can achieve better measurement sensitivity and accuracy. In this talk, we will demonstrate MME as a powerful tool for nanoimprinted grating structure metrology. We will show that MME-based scatterometry at least has the following three aspects of advantages over conventional ellipsometric scatterometry.

(1) More accurate characterization of line width, line height, sidewall angle, and residual layer thickness of nanoimprinted grating structures can be achieved by performing MME measurements in the optimal configuration. In contrast, conventional ellipsometric scatterometry can only be conducted in the planar diffraction configuration, i.e., with the plane of incidence perpendicular to grating lines, which is not necessarily the optimal measurement configuration for nanostructures in general.

(2) Not only further improvement in the measurement accuracy and fitting performance can be achieved, but also the residual layer thickness variation over the illumination spot can be directly determined by incorporating depolarization effects into the interpretation of measured data. The depolarization effects, which are demonstrated to be mainly induced by the finite bandwidth and numerical aperture (NA) of the instrument, as well as the residual layer thickness variation of the nanoimprinted grating structures, can be only handled by MME.

(3) Conventional ellipsometric scatterometry has difficulties measuring asymmetric grating structure due to the lack of capability of distinguishing the direction of profile asymmetry. In contrast, MME not only has good sensitivity to both the magnitude and direction of profile asymmetry, but also can be applied to accurately characterize asymmetric nanoimprinted gratings by fully exploiting the rich information hidden in the measured Mueller matrices.

3:20pm **EL+AS+EM+MC+SS-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films with Forward Calculated Uniaxial Response Simulation**, ***Chad Briley***, *T. Hofmann*, University of Nebraska-Lincoln, *D. Schmidt*, National University of Singapore, *E. Schubert, M. Schubert*, University of Nebraska-Lincoln

We present the vector magneto-optical generalized ellipsometric (VMOGE) response and forward calculated simulations of ferromagnetic slanted columnar thin films. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on slanted columnar thin film samples of permalloy grown by glancing angle deposition passivated by an atomic layer deposited Al2O3 conformal coating. Model analyses of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determines the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor reveal a uniaxial magnetic response of the thin film along the long axis of the columns. The magnetic response was subsequently modelled by a best match model process with uniaxial hysteretic response governed by the shape induced anisotropy from the physical geometry and orientation of the nano-columns. By using model parameters for normalized saturation ||Ms||=1, coercivity ||Hc||=50 mT, and remenance ||Mr||=0.9999*||Ms|| the forward calculated magnetic simulations described the observed magneto-optical response for all measured orientations of the nano-columns with respect to all magnetizing field directions generated by the vector magnet.

1) D. Schmidt, C. Briley, E. Schubert, and M. Schubert Appl. Phys. Lett. 102, 123109 (2013)

4:00pm **EL+AS+EM+MC+SS-ThA6 *In Situ* Generalized Ellipsometry Characterization of Silicon Nanostructures during Lithium-ion Intercalation**, ***Derek Sekora***, *R.Y. Lai, T. Hofmann, M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Nanostructured silicon has emerged as a leading candidate for improved lithium-ion battery electrode design. The combined highly accessible surface area and nanoscale spacing for volumetric lattice expansion of nanostructured thin films have shown improved cycle lifetime over bulk-like silicon films. Additionally, ultra-thin passivation layers have been reported to increase the longevity and stability of silicon thin film electrodes. Very little *in-situ* information has been reported on silicon films during the complicated lithiation process. Furthermore, what information available has been limited to the study of bulk-like thin films. The advantageous geometry of glancing angle deposited (GLAD) thin films allows for the strain from lithiation to affect individual nanostructures in comparison to the bulk response. For this reason, alumina passivated GLAD silicon films were grown for use as working electrodes in half cell electrochemical experiments.

The spatially coherent silicon GLAD nanostructures have intrinsic biaxial optical properties. Therefore, generalized ellipsometry was employed to investigate the silicon film's physical response to lithium intercalation during an electrochemical cyclic voltammagram cycled against pure lithium metal in a conductive anhydrous electrolyte solution. *In-situ* ellipsometric monitoring of directional optical constant changes determined by the homogeneous biaxial layer approach are presented. The optical response expresses a morphologic conversion from a highly anisotropic film to a pseudo-isotropic lithium concentrated form and subsequently, its return to the original anisotropic state. The ability to nondestructively monitor complex nanostructured thin films during lithium-ion processes provides new avenues for high storage battery electrode design.

4:20pm **EL+AS+EM+MC+SS-ThA7 Characterization of SiO_2 Nanoparticle Layers on a Glass Substrate by Spectroscopic Imaging Ellipsometry and AFM**, ***Peter H. Thiesen***, Accurion GmbH, Germany, *G. Hearn,* Accurion Inc., *C. Röling*, Accurion GmbH, Germany

The well-directed organization of nanoparticles is of increasing technical and scientific interest. One approach is the organization of nanoparticles at the air/water interface for applications, like producing 2D colloidal crystals or nanowires. For example, Gil et al. (2007) monitored the formation of 2D colloidal crystals by Langmuir–Blodgett technique. They used Brewster angle microscopy to observe the film quality. Zang et al. (2009) have also studied silica nanoparticle layers at the air/water interface by multiple angle of incidence ellipsometry. For data interpretation, a two-layer model was introduced. With this model, the radius of interfacial aggregates and the contact angle of the nanoparticle surface at the air/water interface were obtained.

In this paper d ifferent line shaped pattern of SiO_2 nanoparticles were characterized by spectroscopic imaging ellipsometry in the wavelength range between 360 and 1000 nm and by AFM. The samples were provided by the research group of Professor Y. Mori, Doshisha University, Japan.

The work shows the unique capability of imaging ellipsometry in characterizing patterned surfaces. We started with a pre inspection of the surface by imaging ellipsometric contrast microscopy. Tiny regions of interest (ROIs) were placed on interesting areas like on different steps of the stripes and Delta and Psi spectra were recorded. The next step in characterization was the mapping of Delta and Psi with pixel resolution of the detector. The same samples were also characterized with an AFM. The results optical modelling are in good agreement with the results of the scanning method.

A. Gil, M. Vaupel, F. Guitiana, D. Möbius (2007) *Journal of Materials Chemistry* **17**: 2434–2439.

D. Zang, A. Stocco, D. Langevin, B. Weib, B.P. Brinks (2009) *Phys. Chem. Chem. Phys.***11**: 9522–9529.

5:00pm **EL+AS+EM+MC+SS-ThA9 Dielectric Tensor Model for Inter Landau-level Transitions in Highly Oriented Pyrolytic Graphite and Epitaxial Graphene – Symmetry Properties, Energy Conservation and Plasma Coupling**, ***Philipp Kühne***, Linköping University, Sweden, *T. Hofmann, M. Schubert,* University of Nebraska-Lincoln, *C.M. Herzinger,* J.A. Woollam Co., Inc., *V. Darakchieva*, Linköping University, Sweden

We report on polarization sensitive, magneto-optic, reflection-type Landau level (LL) spectroscopy at low temperatures by using the integrated optical Hall effect instrument[1] in the mid-infrared spectral range (600 – 4000 cm^{-1}) on highly oriented pyrolytic graphite (HOPG) and epitaxial graphene grown on C-face silicon carbide by thermal decomposition. In both sample systems we observe a multitude of inter-LL transitions. Inter-LL transitions in HOPG possess polarization mode mixing polarization selection rules characteristics, while polarization mode conserving and polarization mode mixing inter-LL transitions are observed in epitaxial graphene which can be assigned to single- and Bernal stacked (ABA) multi-layer graphene, respectively.[2] We present a new dielectric tensor model for inter-LL transitions which explains all experimentally observed line-shapes. For inter-LL transitions in multi-layer graphene and HOPG we employ this new model together with energy conservation considerations, to show that these polarization mode mixing inter-LL transitions couple with a free charge carrier plasma. Finally, inter-LL transition energy parameters are determined and discussed.

[1]) P. Kühne, et. al., Rev. Sci. Instrum., accepted (2014)

[2]) P. Kühne, et. al., Phys. Rev. Lett. **111**, 077402 (2013)

5:20pm **EL+AS+EM+MC+SS-ThA10 Characterization of Exfoliated 2D Nano Materials with Imaging Spectroscopic Ellipsometry**, *P.H. Thiesen,* Accurion GmbH, Germany, ***Greg Hearn***, Accurion Inc., *B. Miller,* Technische Universität München, Germany, *C. Röling,* Accurion GmbH, Germany, *U. Wurstbauer,* Columbia University, *E. Parzinger, A.W. Holleitner, U. Wurstbauer*, Technische Universität München, Germany

In the initial period of graphene research, the issue was to identify and characterize crystallites of microscopic scale. Imaging ellipsometry is a nondestructive optical method in thin film metrology with a lateral resolution down to 1 µm. In a number of papers, Imaging ellipsometry has been applied to characterize graphene flakes of few micrometer size. Ellipsometric contrast micrographs, delta and Psi maps as well as wavelength spectra [1],[2] and single layer steps in multilayer graphene/graphite stacks [3] have been reported.

Molybdenum disulfide is a layered transition metal dichalcogenide. From the point of current research, 2D-nano materials based on MoS_2 are very promising because of the special semiconducting properties. The bulk material has an indirect 1.2 eV electronic bandgap, but single layer MoS_2 has a direct 1.8 eV bandgap. The monolayer can be used in prospective electronic devices like transistors (MOSFETs) or photo detectors. Delta and Psi Spectra of MoS_2 monolayers as well as maps of the ellipsometric angles will be presented. The practical aspect of single layer identification will be addressed and the capability of ellipsometric contrast micrographs as a fast tool for single layer identification will be demonstrated.

An additional focus will be on the modelling of the optical properties of 2D nanomaterials.

[1] Wurstbauer et al., Appl. Phys. Lett. 97, 231901 (2010)

[2] Matkovic et al. J. Appl. Phys. 112, 123523 (2012)

[3] Albrektsen O. J. OF Appl. Phys. 111, 064305 (2012)

Helium Ion Microscopy Focus Topic
Room: 316 - Session HI+2D+AS+MC-ThA

Nanoengineering with Helium Ion Beams
Moderator: Armin Gölzhäuser, University of Bielefeld, Germany, David C. Joy, University of Tennessee, Oak Ridge National Laboratory

2:20pm **HI+2D+AS+MC-ThA1 Helium Ion Microscopy (HIM) Technology for Imaging, Characterization, and nano-Fabrication for nano-Device Materials and Structures**, ***Shinichi Ogawa***, NeRI, AIST, Japan **INVITED**

Several unique applications of a helium ion microscopy (HIM) technology have been studied. In comparison with electron, helium ion has larger cross section, and it realized HIM observation with less current because of higher efficiency of secondary electron generation with maximum distribution energy of 1 eV [1], a few eV in a SEM case, for imaging, which results in less power implant (less thermal damage input) into samples. Utilizing these features, a low dielectric constant material pattern of 70 nm line with less deformation (thermal damage) and a Cu metal line underneath a 130 nm dielectric of band gap of a few eV were imaged [2]. Luminescence from a SiO_2 sample was detected at imaging conditions [3], in which no damage was observed by a transmission electron microscopy (TEM) - electron energy loss spectroscopy method [4]. As one of nano-fabrication applications, we found that a helium ion irradiation using the HIM functionalizes a gate control of carrier conduction in a single-layer graphene at an appropriate amount of helium ion dose to graphene which enable gate bias control of current with an on-off ratio of two orders of magnitude at room temperature [5], [6]. A few nm diameter tungsten particles were deposited onto a TEM sample under the helium ion beam irradiation in $W(CO)_6$ gas atmosphere with high special resolution accuracy, which realized precise electron tomography and re-construction [7], and tungsten pillars of a few um height with 40 nm diameter were formed with a straight hole of a few nm diameter through a center of the pillars [8]. The research on graphene material is granted by JSPS through FIRST Program initiated by CSTP.

References: [1] Y. V. Petrov, O.F. Vyvenko, and A. S. Bondarenko, J. Surface Investigation, 792 (2010), [2] S. Ogawa, W. Thompson, L. Stern, L. Scipioni, L. Notte, L Farkas, and L. Barriss, Jpn. J. Appl. Phys., 49 04DB12 (2010), [3] S. Ogawa, T. Iijima, S. Awata, S. Kakinuma, and T. Kanayama, Proc. of International Interconnect Technology Conference (2011), [4] Y. Otsuka, Y. Shimizu, N. Kawasaki, S. Ogawa, and I. Tanaka, Jpn. J. Appl. Phys., 49 111501 (2011), [5] S. Nakaharai, T. Iijima, S. Ogawa, H. Miyazaki, S. Li, K. Tsukagoshi, S. Sato, and N. Yokoyama, Appl. Phys. Express, 5 015101 (2012), [6] S. Nakaharai, T. Iijima, S. Ogawa, S. Suzuki, S. Li, K. Tsukagoshi, S. Sato, N. Yokoyama, *ACS Nano*, 7 (2013) 5694-5700, [7] M. Hayashida, T. Iijima, T. Fujimoto and S. Ogawa, Micron 43, 992-995 (2012), [8] K. Kohama, T. Iijima, M. Hayashida, and S. Ogawa, J. Vac. Sci.Technol. B 31 (3), 031802 (2013)

3:00pm **HI+2D+AS+MC-ThA3 MEMS Temperature Controlled Sample Stage for the Helium Ion Microscope**, ***Jose Portoles***, *P.J. Cumpson*, Newcastle University, UK

The Helium microscope allows the imaging of samples with magnifications beyond those of electron microscopes with the added advantages of directly imaging insulators without being so critically dependent on a need to conductive coating the samples. This facilitates the imaging of for instance organic structures without the need of surface modification. The large depth of focus allows simultaneously focusing details of the sample at different depths. When using a temperature controlled stage this allows the samples to stay focused as thermal expansion produces vertical displacements of the sample surface, however due to the large magnifications in-plane thermal expansions are still an issue. We have investigated a solution based on a thermally actuated X-Y MEMS stage by exploiting the ability of MEMS

actuators to provide smooth electronic control of lateral displacements in the micron range in order to compensate for lateral thermal expansion at the point of observation. The difficulties involved in producing relatively large out of plane displacements with a MEMS device can be neglected due to the large instrumental depth of focus. The device we present has been fabricated using a "silicon on insulator" (SOI) MEMS process, and can be driven at low voltages and currents using a standard vacuum feedthrough to the instrument's analysis chamber and compensate lateral thermal expansion in order to keep any spot on a small specimen in the field of view at high magnifications. The small size of the heating stage makes it rapid in its thermal response.

3:20pm **HI+2D+AS+MC-ThA4 Monte Carlo Simulations of Focused Neon Ion Beam Induced Sputtering of Copper**, ***Rajendra Timilsina****, P.D. Rack,* The University of Tennessee Knoxville*, S. Tan, R.H. Livengood*, Intel Corporation

A Monte Carlo simulation has been developed to model the physical sputtering and nanoscale morphology evolution to emulate nanomachining with the Gas Field Ion Microscope. In this presentation, we will present experimental and simulation results of copper vias milled by a focused neon ion beam. Neon beams with a beam energy of 20 keV and a Gaussian beam profile with full-width-at-half-maximum of 1 nm were simulated to elucidate the nanostructure evolution during the physical sputtering of high aspect ratio features. In this presentation we will overview our simulation attributes which includes an evolving real-time sputtered via profile considering both thesputtered and re-deposited material. The sputter yield and sputter profile vary with the ion species and beam parameters and are related to the distribution of the nuclear energy loss in the material. We will also illustrate how the effective sputter yield is aspect-ratio dependent due to the change in the effective escape angle of the sputtered species. Quantitative information such as the sputtering yields, dose dependent aspect ratios and resolution-limiting effects will be discussed. Furthermore, we will show that the calculated nuclear energy loss and implant concentration ahead of the sputtering front correlates to observed damage revealed by transmission electron microscopy.

4:00pm **HI+2D+AS+MC-ThA6 Circuit Edit Nanomachining Study using Ne+ & He+ Focused Ion Beam**, ***Richard Livengood****, S. Tan*, Intel Corporation **INVITED**

FIB nanomachining has been used extensively for over 20 years for the purpose of rewiring integrated circuits to validate design changes, isolate process faults, and generate engineering samples. During this time frame, the minimum feature size of an IC (Moore's Law) has scaled from 500nm to 14nm (36X) compared with ~6X scaling of Ga+ FIB. As a result FIB nanomachining capabilities have been steadily erroding over the last several generations, limiting the types of circuit modifications that can be sucessfully completed. There are however, several promising new ion beam scaling R&D initiatives that provide hope of enabing further nanomachining scaling into the sub 10nm process node.

One such technology is GFIS (gas field ion source) technology. He+ GFIS based FIBs have been successfully used to image with sub 0.5nm resolution and nanomachine sub 10 nm structure in Au, Graphine, and other thin film structures.[1, 2, 3] More recently He+ and Ne+ GFIS sputtering properties have been studied for nanomachining in bulk semiconductor films.[4] In this paper, we will show our latest results on GFIS FIB GAE (gas assisted etch) nanomachining and IBID properties and electrical invasiveness impact.

References

[1] J. Notte, M. Rahman, L. Farkas, S. Tan, and R. Livengood, Scanning 33, 1 (2011).

[2] D. S. Pickard, V. Viswanathan, M. Bosman, J. Dorfmüller, H. Giessen, Z. Ai, H. Hao, M. Mahmoudi, Yue Wang and Chao Fang, Invited talk, EIBPN-HIM Session (2012)

[3] V. Sidorkin, E. v. Veldhoven, E. v der Drift, P. Alkemade, H. Salemink, D. Mass, J. Vac. Sci. Technol. B 27 (4) (2009)

[4] S. Tan, R. Livengood, D. Shima, P. Hack, R. Hallstein, J. Notte, and S. McVey, JVST B, 29 (6), 06F604 (2011).

4:40pm **HI+2D+AS+MC-ThA8 Evaluation of EUV Resist Performance below 20-nm CD using Helium Ion Lithography**, *D.J. Maas,* TNO Technical Sciences, Netherlands*, **Nima Kalhor**,* TU Delft, Netherlands*, W. Mulckhuyse, E. van Veldhoven,* TNO Technical Sciences, Netherlands*, A. van Langen–Suurling, P.F.A. Alkemade,* TU Delft, Netherlands*, S. Wuister, R. Hoefnagels, C. Verspaget, J. Meessen, T. Fliervoet*, ASML, Netherlands

For the introduction of EUV lithography, development of high performance EUV resists is of key importance. This development involves studies into sensitivity, resolving power and pattern uniformity. We have used a sub-nanometer-sized 30 keV helium ion beam to expose chemically amplified (CAR) EUV resists.

There are remarkable similarities in the response of resists to He^+ ions and EUV photons. Both primary particle beams traverse the resist and meanwhile interact with the target atoms. The low backscattering of the He^+ ions results in ultra-low proximity effects, which is similar to EUV exposure s . Absorption of an EUV photon creates a high-energy electron that relaxes by the excitation of Secondary Electrons (SEs). A collision of a 20-30 keV helium ion with a target atom directly releases low-energy SEs. Each ion scatters several times in the resist layer, thus enabling resist exposures at very low doses per CH . The energy spectra of SEs generated by EUV and He^+ are remarkably alike. These SEs, in turn, activate the resist.

In this paper we show 30 keV He^+ ions exposures of contact holes and lines with a CD of 8 – 30 nm at 20 nm half-pitch in a chemically amplified EUV resist. We will demonstrate the potential of using He^+ ion lithography [1,2] in the study of EUV resists.

[1] V. Sidorkin et al., *Sub-10-nm nanolithography with a scanning helium beam*, J. Vac. Sci. Technol. B **27**, L18 (2009)

[2] D. Maas et al., *Evaluation of EUV resist performance below 20nm CD using helium ion lithography,* SPIE Proc. **9048**, 90482Z (2014)

5:00pm **HI+2D+AS+MC-ThA9 Helium Ion Beam Lithography for Nanoscale Patterning**, *X. Shi,* University of Southampton, UK*, D.M. Bagnall,* University of New South Wales, UK*, **Stuart Boden***, University of Southampton, UK

Electron beam lithography (EBL), the modification of thin films of resist by a focused beam of electrons to create a pattern that is subsequently transferred into the substrate, is a key technology in the development of nanoscale electronic devices. However, with the demand for ever smaller features and pattern dimensions, new lithographic techniques are required to extend beyond existing limits of EBL. One such emerging technology is helium ion beam lithography (HIBL), driven by the development of the helium ion microscope, a tool capable of producing a high intensity beam of helium ions focused to a sub-nanometer spot [1]. Preliminary studies on HIBL using typical EBL resist materials such as PMMA and HSQ have shown that HIBL has several advantages over EBL, including a smaller spot size (potentially leading to higher resolution patterning) and a decrease in the exposure dose required and so the potential for faster pattern definition and therefore higher throughput. Furthermore, proximity effects, which are caused by beam scattering leading to inadvertent exposure of surrounding material, and are problematic when producing high density patterns in EBL, are massively reduced in HIBL [2], [3].

Here, the latest results from an experimental investigation into the HIBL technique will be presented. Areas of PMMA films of various thicknesses are exposed to different helium ion doses. After subsequent development in MIBK/IPA, atomic force microscopy is used to measure residual layer thickness in order to generate exposure response curves for different initial thicknesses of resist. High sensitivity is confirmed with full exposure of 50 nm thick layers achieved with a helium ion dose of only ~2 $\mu C/cm^2$. Experiments to characterise minimum feature size and proximity effects are currently underway. The use of other high resolution resists will also be investigated with the aim of providing a thorough assessment of the capabilities and limitations of this emerging nano-patterning technique.

[1] L. Scipioni, L. A. Stern, J. Notte, S. Sijbrandij, and B. Griffin, "Helium Ion Microscope," Adv. Mater. Process., vol. 166, pp. 27–30, 2008.

[2] 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, and K. K. Berggren, "Scanning-helium-ion-beam lithography with hydrogen silsesquioxane resist," J. Vac. Sci. Technol. B., vol. 27, no. 6, pp. 2702–2706, 2009.

[3] V. Sidorkin, E. van Veldhoven, E. van der Drift, P. Alkemade, H. Salemink, and D. Maas, "Sub-10-nm nanolithography with a scanning helium beam," J. Vac. Sci. Technol. B., vol. 27, no. 4, p. L18, 2009.

5:20pm **HI+2D+AS+MC-ThA10 Sub-100nm Nanofabrication using Helium and Neon Ion Beams**, ***James Sagar****, C. Nash, N. Braz, T. Wootton, M.J.L. Sourribes, T.-T. Nguyen, R.B. Jackman, P.A. Warburton*, London Centre for Nanotechnology, UK

Sub-100nm Nanofabrication using Helium and Neon Ion Beams

J. Sagar[1], C. R. Nash[1], N. Braz[1,2], T. Wootton[1,2], M. J. L. Sourribes[1,2], T.-T. Nguyen[1,2], R. B. Jackman[1,2], and P. A. Warburton[1,2]

[1]London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London, WCH1 0AH, UK

[2]Department of Electrical and Electronic Engineering, University College London, London, WC1E 7JE, Uk

Using a Zeiss Orion NanoFab we have created sub-100nm devices for experiments in quantum electronics and nanophotonics. The Orion NanoFab has the ability form an ion beam with either helium or neon gas. This makes the Nanofab a much more versatile instrument for nanofabrication since large area mills can be performed using Ne without the need for a Ga FIB column. The use of a Ne gas field ion source (GFIS) in the Orion NanoFab allows fabrication of sub-100nm devices on timescales comparable to that of conventional liquid Ga FIB but with considerably enhanced fidelity due to an increased sputter yield (ten times greater than that of He) whilst retaining a small probe size ($\leq$ 5nm). Using a Ne ion beam we have fabricated two kinds of nanoscale superconducting devices: a superconducting nanowire based on a compound low-T_C superconductor; and an array of nanoscale Josephson junctions based on a compound oxide high-T_C superconductor. The use of an inert-gas ion species in these devices is extremely important as Ga implantation into superconducting materials has previously been shown to suppress superconductivity. The extremely small probe size of the He GFIS has allowed us to create sub-20nm apertures in a variety of materials. Sub-20nm apertures in InAs nanowires and in graphene have been fabricated for experiments in quantum coherent electronics and quantum nanophotonics respectively.

Applied Surface Science
Room: 316 - Session AS+MC+SS-FrM

Practical Surface Analysis II
Moderator: Steven Pachuta, 3M Company

8:20am **AS+MC+SS-FrM1 Vector Potential Photoelectron Microscopy**, ***Raymond Browning***, R. Browning Consultants

Vector potential photoelectron microscopy (VPPEM) is a new class of synchrotron based analytic spectromicroscopy using NEXAFS and XPS spectroscopy. To optimize the spatial resolution VPPEM images very low energy photoelectrons which poses both challenges and opportunities. At low energies the NEXAFS signals have an information depth that is similar to that from total yield absorption (TAY) measurements, while the XPS signals have a variable information depth from the universal curve at low energies. VPPEM has a very high depth of focus, and immunity to many imaging artifacts such as surface charging, and magnetic state. This makes VPPEM suitable for analyzing real world samples, and we present some results from the prototype instrument at NSLS.

8:40am **AS+MC+SS-FrM2 Hydrogen and Chemical Quantification of an Organic Coating**, ***Paul Mack***, Thermo Fisher Scientific, UK

Zinc-coated steel substrates often have an additional organic coating applied, protecting the steel surface or altering its appearance for decorative reasons. X-ray Photoelectron Spectroscopy (XPS) is an analysis technique which provides chemical bonding information from the top few nanometres of a surface down to many microns in depth. It is the ideal technique, for example, for identifying the carbon functional groups in these organic coatings. XPS cannot detect hydrogen, however, but the complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) is able to both detect and quantify hydrogen. REELS can also be used to discern between aliphatic and aromatic carbon in the organic coatings.

There is also a requirement for compositional profiling of these coatings, combining the excellent depth resolution and chemical specificity of XPS with some kind of ion beam sputtering. Traditional methods such as argon monomer ion profiling can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials. Numerous studies over recent years, however, has shown that argon cluster beams may be used for depth profiling while preserving chemical information during analysis of organic materials.

This talk will present data from cluster profiling studies of an organic coating on steel. The data will be compared with an alternative method of profiling the coating, i.e. ultra low angle microtomy. A complete elemental compositional profile of the coating, including hydrogen, will be presented.

9:00am **AS+MC+SS-FrM3 Mechanical Strain Induced Tunable Reflective and Conducting Silver Nanorods Embedded PDMS Film**, ***Pratibha Goel****, *J.P. Singh*, Indian Institute of Technology, India

The formation of metallic films on both inorganic and organic polymeric substrate continues to be of substantial interest because of various applications.[1,2] Polymeric supports offer the obvious advantages in weight, flexibility, elasticity, and fragile relative to inorganic support such as glasses, ceramics, or native metal. Silver is a metal of choice as a reflecting material because of its high reflection coefficient (0.93). Silver also has the highest electrical conductivity of all metals at $6.3 \times 10^7 (\Omega m)^{-1}$. However, there are disadvantages of using silver as the reflecting metal. Firstly, silver is a relatively soft metal so that the face of a mirror needs to be carefully protected from mechanical abrasion. Secondly, silver tends to tarnish which diminishes its reflectivity. (Ambient sulfur-containing compounds are a particular problem.) Thirdly, and perhaps the most important, silver(0), as a more passive metal, does not interact strongly with organic functionalities, which means that adhesion of a silver layer on a polymer surface can be a substantial problem.

In this study we present a straightforward two step fabrication of highly adherent, reflective and surface conductive flexible films. First, the Ag nanorods were deposited on the Si (001) substrates by thermal evaporation of silver powder using oblique angle deposition (OAD).[3] Then the thermal curing of the PDMS on the Ag nanorods grown Si wafer leads to the copolymerization yielding a flexible, reflective and conductive silver surface approaching that of the native film. The Fig. 1 shows schematically the route followed for the fabrication of the sample. As prepared sample appear to be highly reflecting and conducting with the reflectance (R) of 64.17 % at 530 nm and sheet resistance (R_s) of 24.03 Ω/sq. Elongation of the sample up to 30% of its original length results into decrease in the reflectance and increase in R_s. Fig. 2 shows the tunability of the R at 531 nm and R_s with respect to the strain applied. Adhesion between the silver nanorods and the polymeric PDMS film was outstanding. No adhesive tapes removed any silver from the surface. Our sample may find potential applications in multifunctional devices where tunability of reflectance and conductivity is desirable through flexibility.

References: 1. N. Hubin, L. Noethe, Science 262 (1993), 1390.

2. L. Yan, X. M. Zhao, G. M. Whitesides, J. Am. Chem. Soc. 120 (1998), 6179.

3. P. Goel, K. Singh, J. P. Singh, RSC Advances 4 (2014),11130.

9:40am **AS+MC+SS-FrM5 Surface Analysis of Electronic Materials**, *R.L. Opila*, ***Kevin Jones***, *J. Church,* University of Delaware, *R. Gupta, V. Pallem, B. Lefevre,* Air Liquide, *X. Lin*, University of Delaware

Surface analysts at the University of Delaware have used a variety of surface analytical techniques to analyze films for electronic materials applications. These films were deposited by a variety of technique including plasma enhanced chemical vapor deposition, molecular organic chemical vapor deposition and atomic layer deposition using precursors synthesized at Air Liquide. Methods of analysis include x-ray photoelectron spectroscopy, scanning Auger electron spectroscopy, time-of-flight secondary ion spectrometry, nano-indentation and synchrotron-based hard x-ray analysis. The advantages of each technique for particular analyses will be discussed.

10:40am **AS+MC+SS-FrM8 Lewis Base Sites on the Nitrogen-Doped Graphite Surfaces Probed by CO_2 Adsorption**, ***Takahiro Kondo***, *R. Shibuya, S. Morohoshi, D. Guo, J. Nakamura*, University of Tsukuba, Japan

Carbon materials have been reported to exhibit unique adsorption property and catalytic activity when they have received specific treatments such as nitrogen doping. For example nitrogen-doped graphene has been reported to show the superior catalytic activity for the oxygen reduction reaction (ORR) in fuel cell [1]. To understand the origin of such specific properties at the atomic scale, we are now trying to examine the relationship among the localized electronic states of the carbon atoms, the adsorption property of the molecule, and the catalytic activity towards ORR by using model catalyst of graphite with surface science techniques. Previously, we have reported based on the scanning tunneling spectroscopy (STS) that the carbon atoms around a pyridinic-nitrogen (N having two N-C bonds) in a highly oriented pyrolytic graphite (HOPG) have occupied localized states near the Fermi level [2]. We consider that such carbon atoms may act as Lewis base sites [2] and may relate to the ORR activity. In this work, we have examined this hypothesis by observing the carbon dioxide adsorption property with temperature programmed desorption (TPD), ORR catalytic activity measurement, and X-ray photoelectron spectroscopy (XPS).

To prepare the pyridinic-nitrogen-doped graphite (pN-HOPG) as the model catalyst, we have firstly cleaved the HOPG at atmosphere and then bombarded it by the nitrogen ion through Ni patterned mask to make edges with N-termination. After the bombardment, the sample was put into HNO_3 solution for 72 hours to remove Ni impurity. The sample was annealed at 900 K for 2 hours in ultrahigh vacuum. XPS spectrum shows that the nitrogen in the prepared sample consists of over 60 % pyridinic-nitrogen, suggesting that nitrogen atoms are dominantly doped at the edges.

In TPD measurements, CO_2 desorption peak was observed at around 370 K from pN-HOPG after the 1000 L CO_2 exposure at 300 K, while no CO_2 desorption peak was observed from clean HOPG. These results indicate that Lewis base sites are formed on pN-HOPG. The same CO_2-TPD results were reproducibly observed by sequential 4 time measurements. This means Lewis base sites on pN-HOPG does not change by the CO_2 adsorption and desorption. Details of CO_2 adsorption properties on pN-HOPG, the relationship with ORR activity and the influence of nitrogen configuration on the carbon atoms in pN-HOPG will be discussed.

[1] L. Qu et al., ACS Nano, 4 (2010) 1321.

[2] T. Kondo, S. Casolo, T. Suzuki, T. Shikano, M. Sakurai, Y. Harada, M. Saito, M. Oshima, M. Trioni, G. Tantardini and J. Nakamura, Phys. Rev. B 86 (2012) 035436.

* **ASSD Student Award Finalist**

11:00am **AS+MC+SS-FrM9 Towards Spin-FETs: Growth and Characterization of Magnetoelectric Chromium Oxide Films on Graphene***, **Sean Stuart**, E. Sachet, J.-P. Maria, J.E. Rowe, D.B. Dougherty,* North Carolina State University*, M. Ulrich*, Army Research Office

Graphene has brought spintronic devices that depend on the ability to transport spin much

closer to realization. Graphene's high carrier mobility and low spin-orbit scattering allow for efficient

spin transport, which has been demonstrated by several publications over useful length scales [1,2].

Further progress toward more sophisticated spintronic devices requires controllable manipulation of

spin polarized charge carriers. A graphene Spin-Field Effect Transistor has been proposed by

Semenov et al [3] that manipulates the spin of charge carriers in a graphene channel by an exchange

interaction with a hypothetical ferromagnetic dielectric. As an alternative that also adds functionality,

we have identified Cr2O3 as a material whose magnetoelectric properties would enable voltage

controlled switching of the exchange interaction. The Magnetoelectric properties of Cr2O3 have been

extensively studied [4], including recent reports of a robust electrically switched magnetic surface

state [5,6].

We used pulsed laser deposition to grow thin Cr2O3 films directly on HOPG. AFM shows a

smooth Cr2O3 film with the hopg topography preserved. X-Ray Diffraction shows that the film has a

(0001) texture for films grown at 300 - 650ºC, which is the strongest orientation of the

magnetoelectric effect. The magnetic polarization of the film can be aligned by magnetoelectric

annealing and locally switched with conducting AFM, the effects of both are observed by magnetic

force microscopy.

[1]. Han, et. Al. J. Mag & Mag. Mat. Vol. 234, Issue 4, (2012)

[2]. Bruno Dlubak, et al. Nat. phys, 8, 557 (2012)

[3]. Y. G. Semenov, et al. Appl. Phys. Lett. 91, 153105 (2007).

[4]. Manfred Fiebig Phys. D: Appl. Phys. 38 R123 (2005)

[5]. X. He, et al. Nat. Mater. 9, 579 (2010).

[6]. N. Wu, et. al., Phys. Rev. Lett. 106, 17 (2011).

11:20am **AS+MC+SS-FrM10 Energy Loss Of Highly Charged Ions Implanted In MOS Dielectric Films***, **Radhey Shyam**, D.D. Kulkarni, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik*, Clemson University

Energy loss measurements of highly charged ions in the low kinetic energy regime have been made using as-grown SiO_2 (170nm) targets. Highly charged Ar^{+Q} ions (Q=4, 8 and 11) with a kinetic energy of 1 keV were used to produced electronic excitations in the oxides. The irradiated regions of the oxide were then encapsulated under a top metallic contact to form metal-oxide-semiconductor (MOS) devices. The devices were probed with capacitance-voltage (C-V) measurements and the extracted flatband voltages from the C-V curves were correlated with ion energy (kinetic and potential).

The C-V results for highly charged ion experiments reveal that the changes in the flatband voltage and slope for implanted devices relative to the pristine devices can be used to delineate effects due to implanted ions only and ion induced damage. The results confirm that dose as well as and charge-dependent effects can be recorded for irradiation of oxides using this method. In particular, the results as a function of charge state indicate that there is a significant enhancement in the induced flatband voltage shift as the charge state of the beam is increased. This was quantified by measuring the flatband voltage shift across multiple ion doses for fixed incident charge states to obtain a normalized value of the shift induced per incident ion. These normalized results show an enhancement in the shift, which grows monotonically across our charge state data, from 1.14 x 10^{-12} V/ion for Ar^{1+} ions to 1.12 x 10^{-11} V/ion for Ar^{11+} ions. This enhancement in the shift is consistent with the increased potential energy of the higher charge states (e.g. 15 eV for Ar^{1+} and 2004 eV for Ar^{11+}). Viewed as a function of the ion charge state, these data suggest a near-quadratic dependence on the incident charge which is consistent with some theoretical predictions.

Authors Index

Bold page numbers indicate the presenter

— A —

Åhlund, J.: IS+AS+MC+SS-TuM3, 10
Alkemade, P.F.A.: HI+2D+AS+MC-ThA8, 31
Alnabulsi, S.S.: AS+BI+MC+SS-MoA11, **7**; AS+BI+MC-WeA2, 22
Alwine, F.: MC+2D+AP+AS-MoA11, 9
Ammann, M.: IS+AS+MC+SS-WeM10, **21**
Anderson, T.: IS+AS+MC+SS-WeM4, 20
Apblett, C.: IS+AS+MC+SS-WeM4, 20
Arble, C.: IS+2D+MC+NS+SP+SS-WeA11, 24
Axnanda, S.A.: IS+2D+MC+NS+SP+SS-WeA10, 24
Aydogan, P.: MC+2D+AP+AS-MoA7, **9**

— B —

Bagge-Hansen, M.: AS+MC+SS-TuA11, 14
Bagnall, D.M.: HI+2D+AS+MC-ThA9, 31
Balamurugan, B.: AP+AS+MC+NS+SS-ThM12, 25
Baldwin, K.: HI+2D+AS+BI+MC-ThM13, 27
Banerjee, P.: MC+2D+AP+AS-MoA9, 9
Banerjee, S.: MC+2D+AP+AS-MoA9, **9**
Barbacci, D.: HI+2D+AS+BI+MC-ThM13, 27
Barlow, A.J.: AS+BI+MC-WeM6, **19**; AS+MC-MoM6, 1
Barmak, K.: MC+AP+AS-MoM6, **4**
Basile, L.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28
Bates, R.L.: MC-TuP1, **17**
Baur, M.: AS+BI+MC+SS-MoA10, 7
Belenky, G.: MC+AP+AS-MoM4, 3
Belianinov, A.: AS+MC-MoM9, 2
Belu, A.M.: AS+BI+MC-WeA3, **22**
Bergersen, H.: IS+AS+MC+SS-TuM3, **10**
Bersch, E.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Bersuker, G.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Beyer, A.: HI+2D+AS+BI+MC-ThM12, 27
Bielefeld, J.D.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Blackledge, R.: AS+BI+MC-WeA7, 22
Blomfield, C.J.: AS+BI+MC+SS-MoA8, 6; AS+BI+MC-WeA1, 22
Bluestein, B.: AS+BI+MC-WeA9, 23
Bluhm, H.: IS+AS+MC+SS-TuA4, 15; IS+AS+MC+SS-TuM11, 11
Boden, S.A.: HI+2D+AS+MC-ThA9, **31**
Bogdanowicz, J.: MC+AP+AS-MoM1, 3
Borisevich, A,.: AS+MC-MoM9, 2
Boscoboinik, A.: IS+2D+MC+NS+SP+SS-WeA11, 24
Boscoboinik, J.A.: IS+AS+MC+SS-TuM12, **11**
Brannon, H.L.: AS+BI+MC+SS-MoA8, 6; AS+BI+MC-WeA1, **22**
Bravo-Sanchez, M.: AS+MC+SS-TuA8, 14; AS+MC-MoM11, **2**
Braz, N.: HI+2D+AS+MC-ThA10, 31
Briley, C.: EL+AS+EM+MC+SS-ThA4, **29**
Brockman, J.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Brongersma, H.H.: MC+AP+AS-MoM8, **4**
Brown, C.M.: IS+AS+MC+SS-TuA3, **15**
Browning, R.: AS+MC+SS-FrM1, **33**
Bruener, P.: MC+AP+AS-MoM8, 4
Bryan, S.R.: AS+BI+MC+SS-MoA11, 7
Bumm, L.A.: MC+2D+AP+AS-MoA11, 9
Bunch, J.: AS+BI+MC-WeM13, 20
Burgess, J.A.: AS+BI+MC-WeA8, 22
Busby, Y.: MC+AP+AS-MoM5, 4
Bush, B.: AS+BI+MC+SS-MoA9, 7
Bushell, A.: AS+MC-MoM1, 1

— C —

Calley, L.W.: MC+2D+AP+AS-MoA3, 8
Cao, L.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, 12
Carpick, R.W.: AS+BI+MC-WeA12, 23
Castner, D.G.: AS+BI+MC+SS-MoA9, 7
Caubet, P.: MC+AP+AS-MoM10, 4
Ceballos-Sanchez, O.: AS+MC-MoM2, 1
Celano, U.: MC+AP+AS-MoM1, 3
Chan, K.K.: MC+2D+AP+AS-MoA1, 7
Chao: MC+2D+AP+AS-MoA10, 9
Chen, C.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, 12
Chen, F.Z.: MC-TuP7, 17
Chen, X.G.: EL+AS+EM+MC+SS-ThA3, **29**
Cheng, C.-W.: MC+2D+AP+AS-MoA1, 7
Choi, D.: MC+AP+AS-MoM6, 4
Chong, H.: MC-TuP4, 17
Church, J.: AS+MC+SS-FrM5, 33
Clark, K.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28; SP+2D+AS+EM+MC+NS+SS-ThM6, 28
Clavel, M.: MC+AP+AS-MoM11, 5
Clayton, C.R.: IS+AS+MC+SS-TuA12, 16
Coffey, K.R.: MC+AP+AS-MoM6, 4
Cohen, G.: MC+2D+AP+AS-MoA1, 7
Cojocaru-Mirédin, O.: AP+AS+MC+NS+SS-ThM3, **25**
Cook, R.F.: IS+AS+MC+SS-WeM12, 21
Coultas, S.J.: AS+BI+MC+SS-MoA8, 6; AS+BI+MC-WeA1, 22
Counsell, J.D.P.: AS+BI+MC+SS-MoA8, **6**; AS+BI+MC-WeA1, 22
Crumlin, E.J.C.: IS+2D+MC+NS+SP+SS-WeA10, **24**
Cui, J.: AP+AS+MC+NS+SS-ThM12, 25
Cullen, W.G.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, 12
Cumpson, P.J.: AS+BI+MC-WeM6, 19; AS+MC-MoM6, **1**; HI+2D+AS+MC-ThA3, 30
Cutshall, D.B.: AS+MC+SS-FrM10, 34

— D —

Dahanayaka, D.: MC+2D+AP+AS-MoA11, **9**
Darakchieva, V.: EL+AS+EM+MC+SS-ThA9, 30
Das, L.: AS+MC+SS-TuA10, **14**
Deeks, C.: AS+MC+SS-TuA3, **13**
DeHaan, G.A.: AS+BI+MC-WeA8, 22
Demaree, J.: MC+2D+AP+AS-MoA2, **8**
Demeulemeester, J.: MC+AP+AS-MoM1, 3
Deng, W.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28
Deprospo: MC+2D+AP+AS-MoA10, 9
Devaraj, A.: AP+AS+MC+NS+SS-ThM12, 25; AP+AS+MC+NS+SS-ThM6, 25; AS+MC+SS-TuA9, 14
Diebold, A.C.: MC+AP+AS-MoM3, **3**; MC-TuP4, 17
DiStefano, J.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Dollery, C.T.: AS+BI+MC-WeM13, 20
Donetsky, D.: MC+AP+AS-MoM4, 3
Dougherty, D.B.: AS+MC+SS-FrM9, 34
Durand, C.P.: SP+2D+AS+EM+MC+NS+SS-ThM10, **28**; SP+2D+AS+EM+MC+NS+SS-ThM11, 28
Durke, E.M.: AS+MC-MoM10, **2**
Durr, M.: AS+BI+MC+SS-MoA10, **7**

— E —

Eddy, C.R.: MC+2D+AP+AS-MoA4, 8
Eichelbaum, M.: IS+AS+MC+SS-TuM1, 10
Espinosa-Magaña, F.: AS+MC-MoM11, 2
Eyben, P.: MC+AP+AS-MoM1, 3

— F —

Feenstra, R.M.: SP+2D+AS+EM+MC+NS+SS-ThM6, 28
Feigelson, B.N.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, 12
Feldman, L.C.: HI+2D+AS+BI+MC-ThM13, 27
First, P.N.: SP+2D+AS+EM+MC+NS+SS-ThM3, **27**
Fisher, G.L.: AS+BI+MC+SS-MoA11, 7; AS+BI+MC-WeA2, **22**
Fitzpatrick, J.: HI+2D+AS+BI+MC-ThM10, **27**
Fliervoet, T.: HI+2D+AS+MC-ThA8, 31
Fowlkes, J.: SP+2D+AS+EM+MC+NS+SS-ThM10, 28
Franquet, A.: MC+AP+AS-MoM1, 3
French, B.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, **12**
French, M.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Frenkel, A.: IS+AS+MC+SS-WeM3, 20
Frese, N.: HI+2D+AS+BI+MC-ThM12, **27**
Fuhrer, M.S.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, 12
Fujita, D.: HI+2D+AS+BI+MC-ThM6, 26

— G —

Gaddipati, P.: MC+2D+AP+AS-MoA4, 8
Gamble, L.J.: AS+BI+MC-WeA9, **23**
Gaskill, D.K.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, 12
Gassilloud, R.: MC+AP+AS-MoM10, 4
Gebhardt, C.R.: AS+BI+MC+SS-MoA10, 7
Geisler, H.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 13
Gerbig, Y.B.: IS+AS+MC+SS-WeM12, 21
Giles, S.L.: IS+AS+MC+SS-TuA12, 16
Gillen, G.: AS+BI+MC+SS-MoA9, 7
Gilmore, I.S.: AS+BI+MC-WeM13, 20
Goeckner, M.J.: MC-TuP1, 17
Goel, P.: AS+MC+SS-FrM3, **33**
Gölzhäuser, A.: HI+2D+AS+BI+MC-ThM12, 27
Gompf, B.: EL+AS+EM+MC+SS-ThA1, **29**
Goodwin, C.: IS+2D+MC+NS+SP+SS-WeA11, **24**
Gordon, W.O.: AS+MC-MoM10, 2
Gorham, J.M.: AS+BI+MC-WeA11, **23**
Graham, D.: AS+BI+MC-WeA9, 23
Greeley, J.: IS+AS+MC+SS-WeM3, 20
Grehl, T.: MC+AP+AS-MoM8, 4
Groot, I.M.N.: IS+2D+MC+NS+SP+SS-WeA7, **24**
Groover, T.: MC-TuP8, **17**
Gu, G.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28; SP+2D+AS+EM+MC+NS+SS-ThM6, 28
Guo, D.: AS+MC+SS-FrM8, 33
Guo, H.: SP+2D+AS+EM+MC+NS+SS-ThM5, 27
Guo, H.X.: HI+2D+AS+BI+MC-ThM6, **26**
Gupta, R.: AS+MC+SS-FrM5, 33
Gustafsson, T.: HI+2D+AS+BI+MC-ThM13, **27**

— H —

Hammond, J.S.: AS+BI+MC+SS-MoA11, 7; AS+BI+MC-WeA2, 22
Hansen, T.W.: IS+AS+MC+SS-TuA9, 16
Hanson, J.: IS+AS+MC+SS-WeM1, 20
Harrell, W.R.: AS+MC+SS-FrM10, 34
Harriss, J.E.: AS+MC+SS-FrM10, 34
Härtl, G.: AS+MC+SS-TuA7, 14
Hävecker, M.: IS+AS+MC+SS-TuM1, **10**
Havercroft, N.: AS+BI+MC-WeM5, 19
He, G.: SP+2D+AS+EM+MC+NS+SS-ThM6, 28
He, Q.: AS+MC-MoM9, 2
Hearn, G.: EL+AS+EM+MC+SS-ThA10, **30**; EL+AS+EM+MC+SS-ThA7, 30
Heddleston, J.: AS+BI+MC-WeA11, 23
Heine, Ch.: IS+AS+MC+SS-TuM1, 10
Heller, N.W.M.: IS+AS+MC+SS-TuA12, **16**
Hemminger, J.C.: IS+AS+MC+SS-TuA4, 15; IS+AS+MC+SS-TuM11, 11
Herrera-Gomez, A.: AS+MC+SS-TuA8, 14; AS+MC-MoM11, 2; AS+MC-MoM2, **1**
Herzinger, C.M.: EL+AS+EM+MC+SS-ThA9, 30
Hilbert, J.: AS+BI+MC-WeA12, 23

Hipps, K.W.: SP+2D+AS+EM+MC+NS+SS-ThM1, 27
Hite, J.K.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, 12; MC+2D+AP+AS-MoA4, 8
Hoefnagels, R.: HI+2D+AS+MC-ThA8, 31
Hofmann, T.: AS+MC+SS-TuA7, **14**; EL+AS+EM+MC+SS-ThA4, 29; EL+AS+EM+MC+SS-ThA6, 29; EL+AS+EM+MC+SS-ThA9, 30
Holleitner, A.W.: EL+AS+EM+MC+SS-ThA10, 30
Holtmannspötter, J.: AS+MC+SS-TuA7, 14
Hopstaken, M.J.P.: MC+2D+AP+AS-MoA1, **7**
Hsiao, C.N.: MC-TuP7, **17**
Huang, W.: IS+AS+MC+SS-TuM4, **10**
Hudait, M.: MC+AP+AS-MoM11, 5
Huerta-Ruelas, J.A.: AS+MC+SS-TuA8, **14**; AS+MC-MoM11, 2
Hutton, S.J.: AS+BI+MC+SS-MoA8, 6; AS+BI+MC-WeA1, 22

— I —

Idrobo, J.-C.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28
Im, H.: MC+2D+AP+AS-MoA9, 9

— J —

Jablonski, A.: AS+MC-MoM5, 1
Jackman, R.B.: HI+2D+AS+MC-ThA10, 31
Jayanthinarasimham, A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 12; MC-TuP4, **17**
Jesse, S.: AS+MC-MoM9, 2
Jiang, X.: AP+AS+MC+NS+SS-ThM12, **25**
Johnson, M.D.: AS+BI+MC-WeA8, 22
Johnson, N.: MC+2D+AP+AS-MoA7, 9
Jones, K.J.: AS+MC+SS-FrM5, **33**
Jorabchi, K.: AS+BI+MC+SS-MoA4, **6**
Joy, D.C.: HI+2D+AS+BI+MC-ThM1, **26**

— K —

Kalhor, N.: HI+2D+AS+MC-ThA8, **31**
Kalinin, S.V.: AS+MC-MoM9, **2**
Kaltschmidt, B.: HI+2D+AS+BI+MC-ThM12, 27
Kaltschmidt, C.: HI+2D+AS+BI+MC-ThM12, 27
Kambham, A.: MC+AP+AS-MoM1, 3
Kao, J.S.: MC-TuP7, 17
Kaszuba, P.: MC+2D+AP+AS-MoA11, 9
Kayser, S.: AS+BI+MC-WeM5, 19
Kelley, M.J.: AS+MC+SS-TuA10, 14
Kelly, T.F.: AP+AS+MC+NS+SS-ThM1, **25**
Khare, P.: MC-TuP4, 17
Kim: MC+2D+AP+AS-MoA10, 9
Kim, H.: MC+AP+AS-MoM10, 4
Kim, K.: AS+MC+SS-TuA11, 14
King, S.W.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Kling, J.: IS+AS+MC+SS-TuA9, 16
Koleske, D.: AP+AS+MC+NS+SS-ThM5, 25
Kolli, R.P.: AP+AS+MC+NS+SS-ThM13, 26
Kollmer, F.: AS+BI+MC-WeM5, **19**
Kolmakov, A.: IS+AS+MC+SS-TuA3, 15; IS+AS+MC+SS-TuM10, **10**
Komakov, A.: IS+2D+MC+NS+SP+SS-WeA3, 23
Kondo, T.: AS+MC+SS-FrM8, **33**
Kraya, L.Y.: SP+2D+AS+EM+MC+NS+SS-ThM2, 27
Kraya, R.: SP+2D+AS+EM+MC+NS+SS-ThM2, **27**
Kreuzer, H.J.: AP+AS+MC+NS+SS-ThM10, **25**
Kuhn, M.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Kühne, P.: EL+AS+EM+MC+SS-ThA9, **30**
Kulkarni, D.D.: AS+MC+SS-FrM10, 34
Kulkarni, G.R.: AS+MC+SS-TuA9, 14
Kumar, A.: MC+AP+AS-MoM1, 3
Kundu, S.: MC+AP+AS-MoM11, **5**

— L —

LaBella, V.P.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 12; MC-TuP4, 17
LaGoo, L.: AS+BI+MC-WeA3, 22
Lai, R.Y.: EL+AS+EM+MC+SS-ThA6, 29
Lauhon, L.J.: AP+AS+MC+NS+SS-ThM5, **25**
Laursen, T.: MC+2D+AP+AS-MoA6, **8**; MC-TuP3, 17
Le Monge, T.: AS+BI+MC-WeA2, 22
Lechuga, H.: AS+MC+SS-TuA1, 13
Lee, H.D.: HI+2D+AS+BI+MC-ThM13, 27
Lee, J.R.I.: AS+MC+SS-TuA11, 14
Lee, J.U.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 12
Lee, W.T.: MC+2D+AP+AS-MoA10, **9**
Lefevre, B.: AS+MC+SS-FrM5, 33
Leobandung, E.: MC+2D+AP+AS-MoA1, 7
Lherron, B.: MC+2D+AP+AS-MoA10, 9
Li, A.P.: SP+2D+AS+EM+MC+NS+SS-ThM10, 28; SP+2D+AS+EM+MC+NS+SS-ThM11, 28; SP+2D+AS+EM+MC+NS+SS-ThM6, **28**
Lin, X.: AS+MC+SS-FrM5, 33
Lin, Y.: MC+AP+AS-MoM4, 3
Lin, Y.C.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Liu, L.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28
Liu, Q.Q.: IS+2D+MC+NS+SP+SS-WeA9, **24**
Liu, S.Y.: EL+AS+EM+MC+SS-ThA3, 29
Liu, X.: MC+AP+AS-MoM6, 4
Liu, Z.: IS+2D+MC+NS+SP+SS-WeA1, **23**
Liu, Z.L.: IS+2D+MC+NS+SP+SS-WeA10, 24
Livengood, R.H.: HI+2D+AS+MC-ThA4, 31; HI+2D+AS+MC-ThA6, **31**
Lou, J.: SP+2D+AS+EM+MC+NS+SS-ThM10, 28

— M —

Maas, D.J.: HI+2D+AS+MC-ThA8, 31
Mack, P.: AS+MC+SS-FrM2, **33**; AS+MC-MoM1, 1
Madaan, N.: AP+AS+MC+NS+SS-ThM6, **25**; AS+MC+SS-TuA9, 14
Majumdar, A.: MC+2D+AP+AS-MoA1, 7
Makowski, M.J.: IS+AS+MC+SS-TuA4, 15; IS+AS+MC+SS-TuM11, 11
Mangolini, F.: AS+BI+MC-WeA12, **23**
Mani-Gonzalez, P.G.: AS+MC-MoM2, 1
Mannarino, M.: MC+AP+AS-MoM1, 3
Maria, J.-P.: AS+MC+SS-FrM9, 34
Martinez, E.: MC+AP+AS-MoM10, **4**
Martins, B.: SP+2D+AS+EM+MC+NS+SS-ThM5, 27
Mastro, M.A.: MC+2D+AP+AS-MoA4, **8**
Matsubayashi, A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, **12**; MC-TuP4, 17
Matyi, R.: MC-TuP4, 17
Maurya, D.: MC+AP+AS-MoM11, 5
McCarty, K.F.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28
McClimon, J.B.: AS+BI+MC-WeA12, 23
Medikonda, M.: MC+AP+AS-MoM3, 3; MC-TuP4, 17
Meer, T.: AS+MC+SS-TuA7, 14
Meessen, J.: HI+2D+AS+MC-ThA8, 31
Meisenkothen, F.: AP+AS+MC+NS+SS-ThM13, **26**
Meulenberg, R.W.: IS+AS+MC+SS-WeM4, **20**
Meyer, D.J.: MC+2D+AP+AS-MoA4, 8
Michaels, C.A.: IS+AS+MC+SS-WeM12, **21**
Miller, B.: EL+AS+EM+MC+SS-ThA10, 30
Mills, A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, 12
Milošević, M.: AS+MC+SS-TuA3, 13
Möllers, R.: AS+BI+MC-WeM5, 19
Morohoshi, S.: AS+MC+SS-FrM8, 33
Morris, J.R.: AS+MC-MoM10, 2
Morrison, J.: AS+BI+MC-WeA1, 22
Moszkowicz, L.: MC+2D+AP+AS-MoA11, 9
Motoyama: MC+2D+AP+AS-MoA10, 9
Moulder, J.F.: AS+BI+MC+SS-MoA11, 7
Mowll, T.R.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 13
Mulckhuyse, W.: HI+2D+AS+MC-ThA8, 31
Muller, L.: HI+2D+AS+BI+MC-ThM13, 27
Muramoto, S.: AS+BI+MC+SS-MoA9, **7**
Myung, Y.: MC+2D+AP+AS-MoA9, 9

— N —

Najmaei, S.: SP+2D+AS+EM+MC+NS+SS-ThM10, 28
Nakamura, J.: AS+MC+SS-FrM8, 33
Nakayama, T.: MC+2D+AP+AS-MoA6, 8
Nandasiri, M.I.: AP+AS+MC+NS+SS-ThM6, 25; AS+MC+SS-TuA9, **14**
Nash, C.: HI+2D+AS+MC-ThA10, 31
Newberg, J.T.: IS+2D+MC+NS+SP+SS-WeA11, 24
Newman, C.: AS+BI+MC-WeM13, 20
Nguyen, L.T.: IS+AS+MC+SS-TuM4, 10; IS+AS+MC+SS-WeM3, 20
Nguyen, T.-T.: HI+2D+AS+MC-ThA10, 31
Niehuis, E.: AS+BI+MC-WeM5, 19
Nolting, W.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 12
Novak, S.W.: MC+2D+AP+AS-MoA6, 8; MC-TuP3, **17**
Noy, A.: AS+MC+SS-TuA11, 14
Nuhfer, N.T.: MC+AP+AS-MoM6, 4
Nunney, T.S.: AS+MC+SS-TuA3, 13; AS+MC-MoM1, 1

— O —

O'brien, B.: MC-TuP3, 17
Ogasawara, H.: IS+AS+MC+SS-TuM5, **10**
Ogawa, S.: HI+2D+AS+MC-ThA1, **30**
Ohlhausen, J.A.: AS+BI+MC-WeM12, 20
Ong, E.W.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, **13**
Opila, R.L.: AS+MC+SS-FrM5, 33
Osborn, W.A.: AS+BI+MC-WeA11, 23
Osgood, R.M.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA1, **12**
Overzet, L.J.: MC-TuP1, 17

— P —

Pacholski, M.L.: AS+MC+SS-TuA4, **13**
Pachuta, S.J.: AS+MC+SS-TuA1, 13
Pallem, V.: AS+MC+SS-FrM5, 33
Park, D.-G.: MC+2D+AP+AS-MoA1, 7
Park, J.: MC+2D+AP+AS-MoA9, 9; SP+2D+AS+EM+MC+NS+SS-ThM11, **28**; SP+2D+AS+EM+MC+NS+SS-ThM6, 28
Parry, K.: IS+AS+MC+SS-TuA4, 15
Parzinger, E.: EL+AS+EM+MC+SS-ThA10, 30
Passarelli, M.K.: AS+BI+MC-WeM13, **20**
Perrine, K.A.: IS+AS+MC+SS-TuA4, **15**; IS+AS+MC+SS-TuM11, 11
Pfnür, H.: SP+2D+AS+EM+MC+NS+SS-ThM12, **28**
Phelps, R.: MC+2D+AP+AS-MoA11, 9
Piallat, F.: MC+AP+AS-MoM10, 4
Pireaux, J.-J.: MC+AP+AS-MoM5, **4**
Pitters, J.L.: HI+2D+AS+BI+MC-ThM3, **26**; HI+2D+AS+BI+MC-ThM5, 26
Poirier, D.: AS+MC+SS-TuA1, 13
Portoles, J.F.: AS+MC-MoM6, 1; HI+2D+AS+MC-ThA3, **30**
Portz, A.: AS+BI+MC+SS-MoA10, 7
Powell, C.J.: AS+MC-MoM5, **1**
Pratt, H.: IS+AS+MC+SS-WeM4, 20
Priya, S.: MC+AP+AS-MoM11, 5
Prosa, T.J.: AP+AS+MC+NS+SS-ThM13, 26

— R —

Raabe, D.: AP+AS+MC+NS+SS-ThM3, 25
Rack, P.D.: HI+2D+AS+MC-ThA4, 31
Radetić, M.: AS+MC+SS-TuA3, 13
Rading, D.: AS+BI+MC+SS-MoA9, 7; AS+BI+MC-WeM5, 19
Radoičić, M.: AS+MC+SS-TuA3, 13
Raman, S.: MC+2D+AP+AS-MoA9, 9
Rastegar, A.: MC+2D+AP+AS-MoA6, 8
Rehbein, J.: AS+MC+SS-TuA7, 14
Ren, X.: AP+AS+MC+NS+SS-ThM5, 25

Riley, J.: AP+AS+MC+NS+SS-ThM5, 25
Rizzolo, M.: MC-TuP3, 17
Roberts, A.J.: AS+BI+MC+SS-MoA8, 6; AS+BI+MC-WeA1, 22
Robinson, J.A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA3, 12
Robinson, Z.R.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 13
Rockett, A.: MC+2D+AP+AS-MoA7, 9
Rodriguez, J.: IS+AS+MC+SS-WeM1, **20**
Rohrer, G.S.: MC+AP+AS-MoM6, 4
Röling, C.: EL+AS+EM+MC+SS-ThA10, 30; EL+AS+EM+MC+SS-ThA7, 30
Rosowski, F.: IS+AS+MC+SS-TuM1, 10
Ross, P.N.R.: IS+2D+MC+NS+SP+SS-WeA10, 24
Rowe, J.E.: AS+MC+SS-FrM9, 34

— S —

Sachet, E.: AS+MC+SS-FrM9, 34
Sadana, D.K.: MC+2D+AP+AS-MoA1, 7
Sagar, J.: HI+2D+AS+MC-ThA10, **31**
Saidi, B.: MC+AP+AS-MoM10, 4
Sano, N.: AS+BI+MC-WeM6, 19; AS+MC-MoM6, 1
Šaponjić, Z.: AS+MC+SS-TuA3, 13
Sarney, W.L.: MC+2D+AP+AS-MoA2, 8; MC+2D+AP+AS-MoA3, 8; MC+AP+AS-MoM4, **3**
Schamis, M.S.: MC+2D+AP+AS-MoA1, 7
Schamm-Chardon, S.: MC+AP+AS-MoM10, 4
Schlögl, R.: IS+AS+MC+SS-TuM1, 10
Schmidt, D.: EL+AS+EM+MC+SS-ThA4, 29
Schubert, E.: EL+AS+EM+MC+SS-ThA4, 29; EL+AS+EM+MC+SS-ThA6, 29
Schubert, M.: EL+AS+EM+MC+SS-ThA4, 29; EL+AS+EM+MC+SS-ThA6, 29; EL+AS+EM+MC+SS-ThA9, 30
Schultz, J.A.: HI+2D+AS+BI+MC-ThM13, 27
Schürmann, M.: HI+2D+AS+BI+MC-ThM12, 27
Scott, K.: AS+BI+MC-WeA11, 23
Sekora, D.: EL+AS+EM+MC+SS-ThA6, **29**
Senanayake, S.: IS+AS+MC+SS-WeM1, 20
Shan, J.: IS+AS+MC+SS-TuM4, 10; IS+AS+MC+SS-WeM3, 20
Shard, A.G.: AS+BI+MC+SS-MoA6, **6**
Shavorskiy, A.: IS+AS+MC+SS-TuA4, 15
Shen, Z.-X.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA11, **13**
Shi, X.: HI+2D+AS+MC-ThA9, 31
Shibuya, R.: AS+MC+SS-FrM8, 33
Shield, J.: AP+AS+MC+NS+SS-ThM12, 25
Shterengas, L.: MC+AP+AS-MoM4, 3
Shubeita, S.: HI+2D+AS+BI+MC-ThM13, 27
Shutthanandan, V.: AS+MC+SS-TuA9, 14
Shyam, R.: AS+MC+SS-FrM10, **34**
Siegel, D.A.: SP+2D+AS+EM+MC+NS+SS-ThM11, 28
Singh, J.P.: AS+MC+SS-FrM3, 33
Sinha, D.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA8, 12
Slinkman, J.: MC+2D+AP+AS-MoA11, 9
Smeu, M.: SP+2D+AS+EM+MC+NS+SS-ThM5, 27
Sosolik, C.E.: AS+MC+SS-FrM10, 34
Sourribes, M.J.L.: HI+2D+AS+MC-ThA10, 31
Sridhara, K.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA9, **12**
Stacchiola, D.: IS+AS+MC+SS-WeM1, 20
Staib, P.G.: IS+AS+MC+SS-TuA11, **16**
Steel, E.B.: AP+AS+MC+NS+SS-ThM13, 26
Stern, A.C.: IS+AS+MC+SS-TuA4, 15
Stickle, W.F.: AS+BI+MC-WeA8, **22**
Strobel, M.: AS+MC+SS-TuA1, **13**
Strohmeier, B.R.: AS+BI+MC-WeA7, **22**
Stuart, S.C.: AS+MC+SS-FrM9, **34**
Sun, N.: MC-TuP6, 17
Sun, R.: MC-TuP6, **17**
Sun, T.: MC+AP+AS-MoM6, 4
Sun, Y.: MC+2D+AP+AS-MoA1, 7
Suzer, S.: MC+2D+AP+AS-MoA7, 9
Svensson, S.P.: MC+2D+AP+AS-MoA2, 8; MC+2D+AP+AS-MoA3, **8**; MC+AP+AS-MoM4, 3
Szakal, C.: AS+BI+MC-WeM2, **19**

— T —

Tan, S.: HI+2D+AS+MC-ThA4, 31; HI+2D+AS+MC-ThA6, 31
Tanuma, S.: AS+MC-MoM5, 1
Tao, C.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, **12**
Tao, F.: IS+AS+MC+SS-TuM4, 10; IS+AS+MC+SS-WeM3, 20
ter Veen, H.R.J.: MC+AP+AS-MoM8, 4
Thamban, P.L.S.: MC-TuP1, 17
Theilacker, W.: AS+BI+MC-WeA3, 22
Thevuthasan, S.A.: AP+AS+MC+NS+SS-ThM6, 25; AS+MC+SS-TuA9, 14
Thiesen, P.H.: EL+AS+EM+MC+SS-ThA10, 30; EL+AS+EM+MC+SS-ThA7, **30**
Timilsina, R.: HI+2D+AS+MC-ThA4, **31**
Ting, M.: MC+2D+AP+AS-MoA3, 8
Tobias, D.J.: IS+AS+MC+SS-TuA4, 15
Tong, X.: IS+2D+MC+NS+SP+SS-WeA9, 24
Tran, I.C.: AS+MC+SS-TuA11, **14**
Troya, D.: AS+MC-MoM10, 2
Trunschke, A.: IS+AS+MC+SS-TuM1, 10
Tselev, A.: IS+2D+MC+NS+SP+SS-WeA3, **23**
Tunuguntla, R.: AS+MC+SS-TuA11, 14
Tyagi, P.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 13
Tyler, BJ.: AS+BI+MC-WeM10, **20**

— U —

Ulrich, M.: AS+MC+SS-FrM9, 34
Unger, W.: AS+MC-MoM8, **2**
Urban, R.: HI+2D+AS+BI+MC-ThM3, 26; HI+2D+AS+BI+MC-ThM5, **26**

— V —

Van Benthem, M.H.: AS+BI+MC-WeM12, **20**
van Buuren, T.W.: AS+MC+SS-TuA11, 14
van Langen–Suurling, A.: HI+2D+AS+MC-ThA8, 31
Van Spyk, M.H.C.: IS+AS+MC+SS-TuA4, 15; IS+AS+MC+SS-TuM11, **11**
van Veldhoven, E.: HI+2D+AS+MC-ThA8, 31
Vandervorst, W.: MC+AP+AS-MoM1, **3**
Varga, T.: AS+MC+SS-TuA9, 14
Vazquez-Lepe, M.O.: AS+MC-MoM11, 2; AS+MC-MoM2, 1
Ventrice, Jr., C.A.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA10, 13
Verspaget, C.: HI+2D+AS+MC-ThA8, 31

— W —

Wacaser, B.A.: MC+2D+AP+AS-MoA1, 7
Wachs, I.E.: IS+AS+MC+SS-WeM5, **21**
Wagner, J.B.: IS+AS+MC+SS-TuA9, **16**
Walker, L.M.: AS+BI+MC+SS-MoA1, **6**
Walker, M.E.: IS+AS+MC+SS-TuA12, 16
Wang, D.: MC+AP+AS-MoM4, 3
Warburton, P.A.: HI+2D+AS+MC-ThA10, 31
Wells, R.: MC+2D+AP+AS-MoA11, 9
Werner, W.S.M.: AS+MC-MoM3, **1**
West, A.: AS+BI+MC-WeM13, 20
Wielunski, L.: HI+2D+AS+BI+MC-ThM13, 27
Wiggins, B.C.: SP+2D+AS+EM+MC+NS+SS-ThM1, **27**
Willey, T.M.: AS+MC+SS-TuA11, 14
Williams, M.D.: MC-TuP8, 17
Wilmsmeyer, A.R.: AS+MC-MoM10, 2
Winograd, N.: AS+BI+MC-WeM3, **19**
Winter, B.: IS+AS+MC+SS-TuA4, 15
Wolkow, R.: HI+2D+AS+BI+MC-ThM3, 26; HI+2D+AS+BI+MC-ThM5, 26; SP+2D+AS+EM+MC+NS+SS-ThM5, **27**
Wong, A.: MC+2D+AP+AS-MoA11, 9
Woodcock, J.: AS+BI+MC-WeA11, 23
Woods, A.S.: HI+2D+AS+BI+MC-ThM13, 27
Wootton, T.: HI+2D+AS+MC-ThA10, 31
Wormington, M.: MC+AP+AS-MoM3, 3
Wright, A.E.: AS+MC-MoM1, **1**
Wuister, S.: HI+2D+AS+MC-ThA8, 31
Wurstbauer, U.: EL+AS+EM+MC+SS-ThA10, 30
Würz, R.: AP+AS+MC+NS+SS-ThM3, 25
Wynne, J.H.: IS+AS+MC+SS-TuA12, 16
Wytiaz, M.J.: IS+AS+MC+SS-TuA12, 16

— X —

Xu, C.: HI+2D+AS+BI+MC-ThM13, 27
Xu, Z.: AP+AS+MC+NS+SS-ThM6, 25

— Y —

Yang, J.C.: IS+AS+MC+SS-TuA7, **15**
Yates, D.L.: MC+AP+AS-MoM6, 4
Yeadon, A.: AS+MC-MoM1, 1
Yeh, J.L.A.: MC-TuP7, 17
Yu, K.M.: MC+2D+AP+AS-MoA3, 8
Yu, X.Y.: AS+BI+MC+SS-MoA3, **6**
Yu, Y.: 2D+AS+HI+MC+NS+PS+SP+SS-TuA4, 12
Yulaev, A.: IS+AS+MC+SS-TuA3, 15

— Z —

Zeng, S.: IS+AS+MC+SS-WeM3, **20**
Zhang, C.W.: EL+AS+EM+MC+SS-ThA3, 29
Zhang, L.: HI+2D+AS+BI+MC-ThM6, 26
Zhang, S.: IS+AS+MC+SS-TuM4, 10; IS+AS+MC+SS-WeM3, 20
Zhang, X.: SP+2D+AS+EM+MC+NS+SS-ThM6, 28
Zheng, H.: IS+AS+MC+SS-TuA1, **15**
Zhou, G.W.: IS+2D+MC+NS+SP+SS-WeA9, 24