Applied Surface Science
Room 101B - Session AS-MoM

Quantitative Surface Analysis: New Ways to Perform Old Tricks

Moderators: Tony Ohlhausen, Sandia National Laboratory, Carl Ventrice, Jr., SUNY Polytechnic Institute

8:20am **AS-MoM1 Quantitative Analysis of Dendrimer-Encapsulated Nanoparticles***, P. Bhattacharya,* University of Dayton Research Institute*; M.H. Engelhard, L. Kovarik, L. Estevez,* Pacific Northwest National Laboratory*; Y.-C. Wang,* University of Washington*; D.R. Baer,* Pacific Northwest National Laboratory*; D.G. Castner,* University of Washington*; **Daniel Gaspar**,* Pacific Northwest National Laboratory **INVITED**

At the nanoscale, quantitatively and accurately measuring material physical and chemical structure remains a fundamental challenge. Many processes essential to energy production or storage, such as catalysis and battery electrochemistry, rely on nanoscale materials with complex three-dimensional structure. In this work, we describe the characterization of ruthenium oxide polyamidoamide (RuO_x-PAMAM) dendrimer-encapsulated nanoparticles (DEN) that have been developed as catalysts for lithium-air batteries. In a lithium-air battery, the RuO_x-PAMAM DENs catalyze the oxygen evolution reaction during charging. The composition and chemical state of the core nanoparticle, and the three-dimensional structure of the DEN are of great interest in understanding and tuning the performance of these materials in Li-air electrochemical cells. X-ray photoelectron spectroscopy (XPS) has become one of the most widely used tools for surface characterization, including quantitative determination of composition. Accurate XPS quantitation requires accurate understanding of electron escape depth, but this information can, in turn, be used for a more detailed understanding of the distribution of elements with depth in a sample. Rudimentary estimates of the electron escape depth in elemental solids have been supplanted by more accurate methods of accounting for chemical differences in electron escape depth. One such tool is the database developed by Powell, et al., called the NIST Database for Simulation of Electron Spectra for Surface Analysis (SESSA), which allows a user to automatically retrieve data needed for a specific practical application and simulate AES and XPS spectra for a multi-layered thin-film or nanoparticle for measurement conditions specified by the user. This database contains extensive sets of data for the physical quantities relevant to AES and XPS. The internal databases are linked to a user interface via a small expert system that allows a user to automatically retrieve data needed for a specific practical application. SESSA can simulate AES and XPS spectra for a multi-layered thin-film sample for measurement conditions specified by the user. In this work, we have used SESSA to help determine the depth distribution of RuO_x and compare to electron microscopy measurements of DEN structure. We have compared the computed model of XPS signal intensity with the experimental measurements.

9:00am **AS-MoM3 Developing a Straightforward Method to Calculate Shell Thicknesses for Core-Shell-Shell Nanoparticles from XPS Data***, **David Cant**,* National Physical Laboratory, UK*; Y.C. Wang, D.G. Castner,* University of Washington*; A.G. Shard,* National Physical Laboratory, UK

There is currently great interest in the study of core-shell and core-multi-shell nanoparticles. XPS, as a highly surface sensitive and quantitative analysis method, is potentially of great use in the characterisation of these nanoparticle systems. In particular, understanding the chemical composition and thickness of nanoparticle shells is of great importance for understanding how a given nanoparticle system may interact with its environment. More complicated structures, such as core-shell-shell systems are now commonly studied, whether in the context of core-shell systems affected by adventitious carbon contamination or systems with a core-shell-shell structure by design, and as such there is a need for analysis methods capable of providing quantitative information on the structures of such systems.

Straightforward methods for the characterisation of planar overlayers *via* the use of XPS have been available for some time[1], however such planar analysis techniques are clearly unsuited to providing reasonable estimates of nanoparticle shell thicknesses. Several methods exist for the quantitative analysis of shells in core-shell nanoparticle systems *via* XPS, including by comparison to simulated data[2,3] or by direct calculation from empirical formulae[4]. While comparison to simulation can also be used to characterise core-shell-shell nanoparticles, such methods typically require specialist software or expertise, and are not necessarily easily applicable by the general practitioner of XPS. As such, it is important to consider whether a simpler technique for core-shell-shell systems, accessible to any analyst, can be conceived. While not as straightforward as for the core-shell case, an empirical formula for the calculation of core-shell-shell nanoparticle shell thicknesses has been developed[5] as an extension to the T_{NP} formula[4] for core-shell nanoparticles. This technique requires no specialist knowledge or software, and with a few iterations converges rapidly upon estimates of shell thickness with a deviation typically lower than the error expected in the estimation of the required electron attenuation lengths.

1. Cumpson, P. J. -*Surf. Interface Anal.***29,** 403–406 (2000).

2. Smekal, W., Werner, W. S. M. & Powell, C. J. -*Surf. Interface Anal.***37,** 1059–1067 (2005).

3. Mukherjee, S., Hazarika, A., Santra, P. K., Abdelhady, A. L., Malik, M. A., Gorgoi, M., O'Brien, P., Karis, O. & Sarma, D. D. -*J. Phys. Chem. C***118,** 15534–15540 (2014).

4. Shard, A. G. -*J. Phys. Chem. C***116,** 16806–16813 (2012).

5. Cant, D. J. H., Wang, Y.-C., Castner, D. G. & Shard, A. G. -*Surf. Interface Anal.***48,** 274–282 (2016).

9:20am **AS-MoM4 Double-Lorentzian Asymmetric Line-shape as a Practical Tool for Peak-fitting Multiplet Structures in XPS Data***, **Alberto Herrera-Gomez**, D. Cabrera-German,* CINVESTAV-Queretaro, Mexico*; J.A. Huerta-Ruelas,* CICATA-Unidad Queretaro, Mexico*; M. Bravo-Sanchez,* IPICYT, Mexico

The peak-asymmetry commonly found in core level photoemission spectra, especially from transition metals and their oxides, has been described in a number of ways. Doniach and Sunjic (DS) [1] proposed that the asymmetry is due to a "combination of the Kondo effect and a transient and singular re-adjustment of the ground state of the entire Fermi gas to the presence of the effective potential of the hole." The argument was done for metals since the phenomenon requires occupation at the Fermi level. The proposed line-shape, which is extensively employed for peak-fitting, has important shortcomings. The form is not integrable (the area under it is infinite) for any possible value of the associated asymmetry parameter. Since integrability is paramount for composition analysis, the DS line-shape can only be employed in qualitative studies. Another proposed source is the divergence of the energy loss function at zero-loss [2]. Although this argument could apply to both metals and insulators, the divergence in turn causes a divergence in the calculated spectrum, forcing the near-zero loss region to be cut during integration.

A very extended view is that the skewedness is caused by the multiplet structure. Each multiplet component is considered as symmetric and the apparent asymmetry is due to the presence of components of different intensities near each other. In this way it has been possible to qualitatively reproduce the main features (satellites) of a number of materials. An excellent example is the work of Fujii et al. [3] for the Fe 2p spectrum for iron in Fe2O3 and in Fe3O4. As shown in their Fig. 3 and 10, the components are many and distributed with no apparent order. Since the intrinsic width of each component is much larger than the separation among them, it is impossible to experimentally resolve them. In addition, it would not make sense to try to construct a "fundamental" asymmetric line-shape.

Thereupon, we present a practical asymmetric line-shape, the double-Lorentzian (DL) [4], that minimizes the number of parameters employed for fitting complex spectra with apparent peak-asymmetries. The fits are clearly superior than those employing DS and also lacks for the integrability problem. Through DL it is possible to fit theoretical spectra, allowing for the quantitative comparison between the predicted and the experimental data.

1. S. Doniach and M. Sunjic, J. Phys. C 3, 285 (1970).

2. A.C. Simonsen, F. Yubero, S. Tougaard. Phys. Rev. B 56, p. 1612 (1997).

3. T. Fujii, F.M.F. de Groot, G. a Sawatzky, F.C. Voogt, T. Hibma, K. Okada. Phys. Rev. B. 59 (1999) 3195–3202.

4. http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf.

9:40am **AS-MoM5 Quantitative Evaluation of the Carbon Hybridization State by Near Edge X-Ray Absorption Fine Structure Spectroscopy**, ***Filippo Mangolini***, University of Leeds, United Kingdom of Great Britain and Northern Ireland; *J.B. McClimon, R.W. Carpick,* University of Pennsylvania

We present a method to determine the carbon hybridization state of carbon-based material using near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Carbon-based materials are of interest due to their exceptional physical and mechanical properties. Characterizing their structure is challenging, but of paramount importance for a wide range of applications.

Of the analytical methods used to characterize the near-surface region of carbon-based materials, carbon 1s NEXAFS spectroscopy is one of the most powerful. However, a critical assessment of the methodology for quantifying the local carbon bonding configuration using NEXAFS data, which is based on the analysis of the sample of interest and of a highly ordered pyrolytic graphite (HOPG) reference sample, is lacking.

In this study [1], the methodology is critically reviewed. Inconsistencies applying this method are found in the literature. A derivation for the correct experimental conditions to be used for acquiring HOPG reference spectra is presented along with the potential sources of uncertainty. Using this, we present a specific method for determining the distribution of carbon hybridization state in a carbon-based material using carbon 1s NEXAFS spectroscopy. As an example, a hydrogenated amorphous carbon film was analyzed. NEXAFS results were compared with results from X-ray photoelectron spectroscopy and Raman spectroscopy. Good agreement was seen, validating our method. This work can assist surface scientists in accurately characterizing the bonding state in carbon-based materials.

1. F. Mangolini, J.B. McClimon, R.W. Carpick, *Anal. Chem.*, 88 (5), 2817, 2016.

10:00am **AS-MoM6 Simultaneous XPS-UPS Depth Profiling of Thin Films**, ***Jon Treacy***, *C. Deeks, P. Mack, T.S. Nunney,* Thermo Fisher Scientific, UK

Thin films have found use in the fields of microelectronics, coatings and photovoltaics, amongst others and continued research is of vital importance in order to improve their performance in these applications. X-ray Photoelectron Spectroscopy (XPS) is a long established technique for analysing these types of samples due to its chemical specificity and surface sensitivity. The closely related technique, Ultraviolet Photoelectron Spectroscopy (UPS), has also been widely utilised to provide detailed valence electronic information with greater surface specificity than XPS, due to the incident radiation being of lower energy.

While useful information is acquired from XPS and UPS in isolation, a more powerful insight into the structure of a material comes from using these two techniques in conjunction, allowing a more complete material characterisation to be performed. Previously, switching between techniques throughout the course of an experiment has been an involved and often laborious process, discouraging more widespread use. Recently the automation of UPS has allowed concurrent acquisition of XPS and UPS data during depth profiling, providing a much sought after insight into the correlation between chemical and electronic structure at within a substrate at various depths.

Of particular interest is the ability to access the valence electronic structure at mixed oxide interfaces using small argon ion gas clusters, which was not previously possible due to the loss of electronic structure in semiconductors or organic materials on exposure to monatomic argon ion beams. This presentation demonstrates the wealth of information that can be acquired by performing XPS-UPS depth profiles and the ease with which this information can be acquired and processed, due to recent instrumentation and software developments.

11:00am **AS-MoM9 Quantification of the Layer Thickness of Thin Organic Layers by Secondary Ion Mass Spectrometry Depth Profiling**, *M.P. Seah,* ***Rasmus Havelund***, *I.S. Gilmore,* National Physical Laboratory, UK

Secondary ion mass spectrometry depth profiling using argon gas cluster sputtering is increasingly applied for the analysis of organic materials including layer stacks used in organic electronic devices. The depth profiles provide valuable information about layer diffusion, segregation, chemical degradation and contaminants in the stack but are generally not quantitative.

We report a study of the quantification of the amount of matter by secondary ion mass spectrometry (SIMS) when depth profiling a nominally 3.1 nm delta layer of fmoc-pentafluoro-L-phenylalanine in Irganox 1010. The depth profiles are made using 5 keV Ar_{2300}^+ sputtering with analysis by 25 keV ions. Data for 89 negative secondary ions shows profiles whose integrated areas, when normalized to the intensity for the pure material, vary over a factor of 12. This variation mainly arises from matrix effects that are measured here using separate samples with mixed layers of 3 intermediate compositions of the two materials. Strong effects can cause the delta layer signal to show structure that may be misinterpreted. The compositional profile is established by using trial profiles, representing the composition, which are then enhanced or reduced according to the measured matrix effect and the result is fitted to the normalized intensity data. It is critical to include the roughening caused by the ion beam. When this is included, the amount of matter is found to be equivalent to 3.25 ± 0.05 nm.

It is concluded that the matrix terms used are a good description of the phenomenon and that SIMS profiles may be made quantitative if suitable secondary ions are available and the matrix terms measured.

11:20am **AS-MoM10 Spectromicroscopy and Vector Analysis of Carbon Materials**, ***Adam Roberts***, Kratos Analytical Limited, UK; *N. Fairley,* Casa Software Ltd, UK; *J.D.P. Counsell, C.J. Blomfield,* Kratos Analytical Limited, UK

Material characterisation by photoelectron spectroscopy is an established technique with a wealth of published data. With the improvement in spectrometer performance spectra are routinely acquired from areas with diameters in the tens of microns, although most routine analysis is performed at much larger areas. Spectra averaged over an analysed area assume a material is homogeneous over this probed area although this might not be true [1,2]. Information from lateral and in-depth distributions [3] for elemental and chemical states on a surface can be probed using XPS imaging either at a single binding (kinetic) energy or over a narrow energy range corresponding to a core-level photoemission peak.

A relatively new and under exploited approach for materials surface characterisation is multispectral XPS imaging, also referred to as spectromicroscopy, where a series of images incremented in energy such that each pixel contains a spectrum. A great advantage of this approach is that spectral information can be reconstructed from defined areas which are smaller than those possible with focused x-ray or virtual probe selected area XPS. Furthermore intensity may be classified by pixel location and binding energy, and summed to reveal multiple spectral forms from a measurement. These spectral forms are ideal for a novel vector method used to identify spectral components characteristic of a material [4,5]. Analysis of the spectra-from-images where the reconstructed spectra are no longer averaged over the total area from which the image is acquired is central to the success of the vector analysis approach. This allows both sample and instrument dependent differences to be ‘removed’ from the data.

Development of data processing to support spectromicroscopy data reduction has been necessary and a number of approaches have been successfully applied in the characterisation of model and real-world samples[6,7]. This approach has been extended to the interpretation of C 1s spectra for carbon based materials from purely sp^2 graphite and a small number of polymeric materials. As part of this study the influence of sputter cleaning such materials using Ar^+ ion gas clusters is also presented.

[1] S. Béchu *et.al* Surf. Interface Anal., 2016,48,301-309

[2] E.F. Smith *et.al* Surf. Interface Anal. 2005, 38, 69-75

[3] J. Walton, *et.al* Surf. Interface Anal. 2016, 48, 164–172

[4] J. Baltrusaitisa, *et.al*, Applied Surface Science 326 (2015) 151–161

[5] M. d’Halluin, *at.al*, 2015 Carbon, 93, 974 -983

[6] J. Walton, *et.al,* Surf. Interface Anal. 2008, 40, 478 - 481

[7] A.J. Barlow *et.al*, Surf. Interface Anal. 2015, 47, 173-175

11:40am **AS-MoM11 Angular Broadening in Core Electron Spectroscopy**, *H. Cohen,* Weizmann Institute of Science, Israel; ***Alon Givon***, Tel Aviv University, Israel

Using an analytic approach, the role of angular broadening in quantitative core-electron spectroscopy is investigated. It is shown why, practically, the broadening effect remains relatively small for a broad range of parameters, including detection angular openings of nearly +- 30 degrees. Based on the analytic expression, a correction factor can be derived, suggesting that the replacement of inelastic-mean-free-path by an effective attenuation-length parameter is not necessarily an optimal choice. The derived expression further proposes useful insight on the contribution of leading experimental parameters and, in particular, on the sharp increase of elastic-scattering corrections above a (depth dependent) critical angle.

Biomaterial Interfaces
Room 101A - Session BI+AS-MoM

Biomolecules and Cells at Interfaces

Moderator: Joe Baio, Oregon State University

8:20am **BI+AS-MoM1 Probing the Selectivity of Antimicrobial Peptides to Cell Membranes by Sum Frequency Generation Spectroscopy***, **Thaddeus Golbek**,* Oregon State University*; J. Franz,* Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany*; J.E. Fowler, K.F. Schilke,* Oregon State University*; T. Weidner,* Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research, Mainz, Germany*; J.E. Baio,* Oregon State University

Cationic amphiphilic peptides have been engineered to target both Gram-positive and Gram-negative bacteria while avoiding lysis of other cell types. However, the exact mechanism of how these peptides target, bind, and disrupt bacterial cell membranes is not understood. One specific peptide that has been shown to selectively capture bacteria is WLBU2 (sequence RRWVRRVRRWVRRVVRVVRRWVRR). It has been suggested that WLBU2 activity stems from the fact that when interacting with bacterial cell membranes the peptide assumes an α-helical structure and inserts itself into the membrane. To test this hypothesis, we applied sum frequency generation (SFG) spectroscopy and surface tensiometry to probe the peptide-lipid-air interface and identify the structure and monitor the interaction of WLBU2 with two model lipid monolayers that mimic mammalian and bacterial cell membranes. Model mammalian cell membranes were built upon zwitterionic 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) lipids while bacterial cell membranes were constructed with negatively charged 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-rac-glycerol) (DMPG) lipids. The rate at which the surface pressure reaches equilibrium is 4.3 times faster for WLBU2 interacting with the negatively charged DMPG lipid monolayer than with the zwitterionic DPPC lipid monolayer. This observed WLBU2 binding affinity preference to negatively charged membranes is likely due to electrostatic interactions between positively charged amino acids within the peptide and negatively charged lipids. SFG studies at the peptide-lipid-air interface demonstrate that binding of WLBU2 induces increased lipid monolayer order. A larger increase in acyl chain order from 2.2 to 3.4 determined by the ratio of the CD_3 symmetric (2075 cm^{-1}) and CD_2 symmetric (2100 cm^{-1}) peak amplitudes suggest that WLBU2 is found at the surface of the zwitterionic phospholipid monolayer and not inserted. The amide I region SFG spectrum of WLBU2 interacting with the zwitterionic lipid monolayer shows two peaks near 1642 cm^{-1} and 1678 cm^{-1} indicative of an inactive β-sheet structure. A peak near 1651 cm^{-1} for WLBU2 interacting with negatively charged lipids is assigned to an active α-helix structure. Altogether, we demonstrate that WLBU2 shows a higher binding affinity to bacterial cell membranes and is in an active α-helix structure, alternatively in the presence of mammalian cell membranes in an inert β-sheet structure.

8:40am **BI+AS-MoM2 Bacterial Adhesion to Immobilized Liquid Layers under Dynamic Conditions***, **Caitlin Howell**,* University of Maine*; Y. Kovalenko, I. Sotiri,* Harvard University*; J. Overton,* University of Maine*; J. Aizenberg,* Harvard University

Immobilized liquid (IL) layers are an emerging technology shown to prevent bacterial biofouling of surfaces. In this work, we show how in one class of IL-coated materials, infused polymers, bacterial adhesion can be strongly dependent on growth conditions. Samples grown with *Escherichia coli* under more relevant dynamic conditions showed significantly increased colony-forming unit counts compared to the same system grown under static conditions. Direct visualization of the surfaces suggested that this was due to a disturbance of the IL layer when exposed to shaking conditions, which allowed more bacteria to remain on the surface after an initial rinse. However, no incorporation of the bacteria into the oil layer was detected. To further investigate the extent of this adhesion, we used sequential removal cycles to gauge the relative adhesion strength of the remaining surface-bound *E. coli*. Through this method, we found that despite no initial difference in adherent CFUs compared to control samples with no IL layers, IL samples did reduce overall adhesion of the bacteria even after incubation under dynamic conditions. Further tests on a flagella-deficient strain of *E. coli* revealed that while flagella play a significant role in adhesion to IL layers, they are not the sole adhesion mechanism for this species. Finally, tests on two other clinically-relevant species of bacteria, *Staphylococcus aureus* and *Pseudomonas aeruginosa*, using similar methods revealed clear species-dependent differences in adhesion after growth under dynamic conditions. These results shed new light on the interaction of bacteria with IL layers, and demonstrate the importance of both relevant growth conditions and thorough analysis to obtaining clear results in these systems.

9:00am **BI+AS-MoM3 Nitric Oxide Materials—An Approach to Creating More Hemocompatible Medical Device Coatings***, **Hitesh Handa**,* University of Georgia **INVITED**

Blood/material interaction is critical to the success of implantable medical devices, ranging from simple catheters, stents and grafts, to complex extracorporeal artificial organs which are used in thousands of patients every day. There are two major limiting factors to clinical application of blood contacting materials: 1) platelet activation leading to thrombosis, and 2) infection. Despite a thorough understanding of the mechanisms of blood–surface interactions, and decades of bioengineering research effort, the ideal non-thrombogenic prosthetic surface remains an unsolved problem. One approach to improving the hemocompatibility of blood-contacting devices is to develop materials that release nitric oxide (NO), a known potent inhibitor of platelet adhesion/activation and also an antimicrobial agent. Healthy endothelial cells exhibit a NO flux of 0.5-4x10^{-10} mol cm^{-2} min^{-1}, and materials that mimic this NO release are expected to have similar anti-thrombotic properties. I will discuss the potential of incorporating NO donor molecules such as diazeniumdiolates or S-nitrosothiols (RSNOs) into various polymers, and their hemocompatibility and antibacterial properties in short-term (4 h) and long-term (7 d) animal models.

9:40am **BI+AS-MoM5 Why do Bacteria Stick to Some Surfaces and Not Others? Characterisation of the Behaviour of Motile Bacteria at and Above the Surface of Materials***, A.L. Hook, A. Carabelli, N.A. Russell, P. Williams, **Morgan Alexander**,* The University of Nottingham, UK

High throughput screening has been used to discover a novel class of polymers with resistance to bacterial attachment and subsequent biofilm formation.[1,2] Physicochemical descriptions of the surfaces have to date been found insufficient to predict the wide range of bacterial attachment across these diverse polymer libraries, and cannot offer an explanation of the controlling phenomena. Whilst perhaps disappointing for the physical sciences, the life sciences are replete with information on how bacteria respond to their local environment, with chemotaxis being one of the most readily observed processes. Unsurprisingly, microorganisms cannot be approximated to inert spheres and rods as they possess surface responsive appendages such as flagella, which enable them to swim, pili that confer twitching motility and fimbriae that mediate surface attachment. These in turn are coupled to sophisticated signal transduction mechanisms that facilitate integration of multiple local environmental parameters at both single cell and population levels. Many of these sensory systems are postulated to contribute to surface sensing. As an example of the complexity of these processes, the opportunistic pathogen *Pseudomonasaeruginosa* has over 60 two-component sensor kinase response regulator systems involved in environmental adaptation.

We believe that bacterial decision-making is key to determining whether a surface is colonised or not. I will present the early results from our optical microscopy investigations of how individual bacterial cells respond to surfaces. We have developed a novel microscope that collects temporal 3D information on cell position using both holography and remote scanning microscopy. [3] Simultaneously surface tracking can be achieved using DIC, TIRF and TIR microscopy. This allows us to track not only the motion of single cells at the surface, but also their approach to and behaviour after contact with the surface.

We will combine these findings with our existing understanding of the surface chemistry-attachment relationships achieved for certain subsets of materials and attachment regimes,[4,5] with chemical analysis of the in situ surface to build a complete description of this complex biointerface and the response of bacteria to it. This information is crucial in determining how bacteria behave with respect to defined surfaces and has important implications for the prevention of device centred infections.

1. Hook et al. Nature Biotechnology 2012
2. Hook et al. Advanced Materials 2013
3. Botcherby et al. Circulation Research 2013
4. Epa et al. Advanced Functional Materials 2014
5. Sanni et al. Advanced Healthcare Materials 2015

10:00am **BI+AS-MoM6 Probing Adhesion of Marine Biofilm Formers by Microfluidics***, K. Nolte,* Ruhr-University Bochum, Germany*; M. Alles, M.P. Arpa-Sancet, C. Christophis,* University of Heidelberg, Germany*; **Axel Rosenhahn**,* Ruhr-University Bochum, Germany

When new Materials are developed to control and influence Biofilm growth, the ability of biofilm formers to firmly adhere to the coatings is one key property. Several techniques have been developed in the past to probe attachment strength of cells [1]. Especially microfluidic test systems [2] offer several advantages, such as small sample area, small amounts of target species, and high throughput. We developed microfluidic assays that allow to test bacterial and diatom adhesion on coatings [3,4]. Cells are driven through a microchannel at a precisely controlled flow rate and at a constant concentration and both, accumulation and detachment can be monitored by video microscopy. Using self-assembled monolayers as model surfaces we were able to show that the adhesion strength correlates with the accumulation dynamics if an appropriate shear stress is applied. Based on this finding, a parallelized microfluidic system has been developed that allows simultaneous, comparative testing of materials. Due to the modular assembly of the setup, not only model surfaces and thin organic films, but also practical coatings can be analyzed.

[1] L. Marcotte, M. Tabrizian, ITBM-RBM 2008, 29, 77

[2] D.P. Bakker, A. van der Plaats, G.J. Verkerke, H.J. Busscher, H.C. van der Mei, Appl. Envir. Microbiol. 2003, 69(10), 6280

[3] M. Arpa-Sancet, C. Christophis, A. Rosenhahn, Biointerphases 2012, 7, 2

[4] M. Alles, A. Rosenhahn, Biofouling. 2015, 31, 469–480.

10:40am **BI+AS-MoM8 Protein Control of Materials Nucleation Probed by Sum Frequency Generation***, **Tobias Weidner**,* Max Planck Institute for Polymer Research, Mainz, Germany

Proteins can act as Nature's engineers at interfaces and manipulate both hard and soft tissue – they shape biominerals, manipulate cell membranes and nucleate materials. Despite the apparent importance for engineers working in the fields of surface engineering, drug delivery, or diagnostics, the molecular mechanisms dictating interfacial protein action have remained largely elusive. Our goal is to probe the structure and structural dynamics of such active proteins – in action at the surface.

Mineral proteins have the ability to control and steer the growth of hard tissue by binding specific mineral facets and precipitating silica and phosphates. They control the intricate mineral morphologies found in diatom cell walls, mollusk nacre, but also human teeth and bone. Inspired by diatom silification we used amphiphilic peptides consisting of leucine and lysine (LK peptides) to investigate biomineralization at surfaces. These peptides can adopt helical or beta sheet structures at the air-water interface. Upon addition of a silica precursor we obtained freestanding peptide-silica hybrid sheets with thicknesses of ~4 nm. We have followed the biomineral composition and interactions between peptides and silica at different early stages of biomineralization using a combination of surface spectroscopies and microscopies. Our experimental findings were complemented with molecular dynamics simulations. Our data shows that the peptide surface folding dictates the nanometer scale morphology of the prepared silica film.[1]

A particularly fascinating example of protein driven nucleation and phase transitions are ice-nucleating proteins. These proteins are used by specific bacteria to attack plants and cause frost damage by growing ice crystals at temperatures that would otherwise not allow ice formation. A recent survey by the NASA found large amounts of biological ice nucleators in the troposphere where they may affect global precipitation patterns. We have followed the interaction of freeze proteins with surrounding water molecules – how specialized protein sites lock water molecules in place and manipulate the flow of energy within the surrounding layers of water.[2]

1 H. Lutz, V. Jaeger, R. Berger, M. Bonn, J. Pfaendtner, T. Weidner

Biomimetic growth of ultrathin silica sheets using artificial amphiphilic peptides

Advanced Materials Interfaces, 1500282 (2015).

2 R. Pandey, K. Usui, R. A. Livingstone, S. A. Fischer, J. Pfaendtner, E. H. G. Backus, Y. Nagata, J. Fröhlich-Nowoisky, L. Schmüser, S. Mauri, J. F. Scheel, D. A. Knopf, U. Pöschl, M. Bonn, T. Weidner

Ice-nucleating bacteria control the order and dynamics of interfacial water

Science Advances, 2 (2016).

11:20am **BI+AS-MoM10 Regulation of Cell Surface Access and Mechanics at the Interface***, **Jennifer Curtis**, P. Chang, W. Wei, L.T. McLane,* Georgia Institute of Technology*; J. Scrimgeour,* Clarkson University **INVITED**

A polymer brush-like structure decorates the cell surface of many cell types ranging from fibroblasts to mesenchymal stem cells to cancer cells. This sugar-rich pericellular matrix (PCM) plays physical and chemical roles in biological processes ranging from brain plasticity, to adhesion dependent processes like cell migration, to the onset of cancer. Here I will report on biophysical and mechanical assays that characterize the structure of the pericellular matrix and its impact on the transport of nanoparticles and molecules to the cell surface. Further, I will present compelling quantitative evidence that hyaluronan polymer expression at the cell-substrate interface tunes cell adhesion strength, working in concert with focal adhesions.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+AS+MI-MoM

Advances in High-Resolution Imaging Techniques (8:20-10:20 am)/Pushing the Limits with X-Ray Spectroscopy (10:40 am-12:00 pm)

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Claus Michael Schneider, Forschungszentrum Juelich GmbH, Germany

9:00am **SA+AS+MI-MoM3 Applications of Novel Hard X-ray Nanoprobe in Nanoscience***, **Gema Martinez-Criado**,* Madrid Materials Science Instititute, CSIC, Spain **INVITED**

Owing to the spatial resolution and sensitivity (i.e., signal to background ratio), nano and micro X-ray beams are emerging tools with a strong impact in nanoscience. Although the optical quality of the X-ray focusing devices has limited the progress of hard X-ray nanoprobes, recent advances in fabrication techniques have pushed the spatial resolution towards the diffraction limit. As a result, the use of nano and micro X-ray beams has begun to extend towards the atomic domain, with concomitant and continuous developments of multiple analytical tools. The study of micro/nanoscale objects, small embedded nanodomains with weak signals and/or heterogeneous structures at the nanometer scales has required the use of intense X-ray pencil beams. Additionally, stimulated by the great brilliance with reduced emittance of current third generation synchrotron sources, and new developments in X-ray detector technology, today intense nano-X-ray beams are available with a variety of focusing devices. Finally, thanks to the multiple interactions of X-rays with matter these X-ray probes can be used for manifold purposes, such as ultra-sensitive elemental/chemical detection using X-ray fluorescence/X-ray absorption, or for identification of minority phases, and/or strain fields by X-ray diffraction with nanometer resolution. In the present talk I describe how hard X-ray nanobeams are produced and exploited today for space-resolved determination of structural and electronic properties, as well as for chemical speciation of nanosized materials. Selected recent examples will range from phase separation in single nanowires to visualization of dislocations and buried interfacial defects, to domain distortions and quantum confinement effects.

10:40am **SA+AS+MI-MoM8 Extreme X-ray Flux to Probe Picosecond Dynamics***, **Alfred Baron**,* RIKEN SPring-8, Japan **INVITED**

Inelastic x-ray scattering (IXS), *in principle*, provides a nearly ideal opportunity to probe dynamics on ps and sub-ps time scales via direct measurement of the dynamic structure factor, S(Q,ω). Such measurements are interesting in many areas of science, including fundamental understanding of liquid behavior, investigations of phonons in complex materials such as superconductors and ferroelectrics, and even to help determine the composition of the earth's interior. However, high-resolution non-resonant IXS measurements are *severely flux limited*.

Over the last 18 years, the author has spearheaded a program to increase the world capability for high-resolution IXS measurements through work at SPring-8 in Japan. This began with designing and constructing a beamline based on a standard insertion device [1] then progressed to a second beamline using 3x5m tandem small-gap insertion devices (IDs) [2], while in parallel, upgrading the earlier facility to a optimized small-gap ID. *This has successfully led to world-leading flux at workhorse spectrometers with ~1.25 meV resolution and 30 GHz onto the sample at 21.7 keV*, and up to 30 momentum transfers collected in parallel. Resolution as good as 0.75 meV [3] can be achieved at higher (25.7 keV) energy while medium resolution spectrometer provides in excess of 2 THz onto a sample with 27 meV resolution for measuring electronic dynamics.

The presentation will discuss aspects of the instrumentation for IXS, and recent sample science. On the instrumentation side, on top of "straightforward" issues such as sub-mK temperature control over >50 channels, installation of more that 30 tons of spectrometer, there were unique and new issues related to operating 3x5m tandem small- (6mm-) gap insertion devices [4]. On the sample side, the talk will highlight recent efforts in geoscience, where measurements at record pressures and temperatures have allowed us to constrain to composition of the Earth's core - both the outer liquid core [5] and the inner solid core. This will be complemented by a short discussion of a surprising phonon anomaly in YBa2Cu3O7-d, where phonon line-widths undergo a remarkable increase below the superconducting transition temperature [7] in what is perhaps the largest phonon anomaly observed to date in the absence of a structural phase transition.

[1] Baron, *et. al.*, J. Phys. Chem. Solids **61**, 461 (2000).

[2] Baron, SPring-8 Inf. Newsl. **15**, 14 (2010).

[3] Ishikawa, *et al*., J. Synch. Rad. **22**, (2015).

[4] Baron, *et al*., AIP Conf. Proc. **SRI2015** (Accepted).

[5] Nakajima, *et al*., Nat Commun. **6**, (2015).

[6] Sakamaki, et al., Sci. Adv. **2**, (2016).

[7] Baron*, et al*., in preparation.

11:20am **SA+AS+MI-MoM10 Beating Complexity through Selectivity: Anti-Stokes Resonant Inelastic X-ray Scattering for Excited State Dynamics***,* ***Alexander Föhlisch,*** University of Potsdam, Germany **INVITED**

Ultrafast electronic and structural dynamics of matter govern rate and selectivity of chemical reactions, as well as phase transitions and efficient switching in functional materials. Since X-rays determine electronic and structural properties with elemental, chemical, orbital and magnetic selectivity, short pulse X-ray sources have become central enablers of ultrafast science. Despite of these strengths, ultrafast X-rays have been poor at picking up excited state moieties from the unexcited ones. With time-resolved Anti-Stokes Resonant X-ray Raman Scattering background free excited state selectivity in addition to the elemental, chemical, orbital and magnetic selectivity of X-rays can be achieved. For low symmetry systems energetically off-set signatures dominate, and for inversion symmetric systems a clear separation between ground and excited states occurs. This unparalleled selectivity extracts low concentration excited state species along ultrafast dynamic pathways. These approaches will benefit from recent advances towards non-linear X-ray matter interaction and an outlook is given how future fourier limited X-ray laser pulses will explore ultrafast dynamics.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-MoM

Advances in Scanning Probe Microscopy

Moderators: Saban Hus, Oak Ridge National Laboratory, Chanmin Su, Bruker Nano

8:20am **SP+AS+MI+NS+SS-MoM1 Ultrafast Imaging of Polarization Switching in Ferroelectrics via Complete Information Acquisition in SPM***,* ***Suhas Somnath****, A. Belianinov, S.V. Kalinin, S. Jesse,* Oak Ridge National Laboratory

SPM imaging can be represented as an information channel between the dynamic processes at the tip-surface junction and the observer. Current SPM techniques use heterodyne detection methods such as lock-in amplifiers which result in significant loss in vital information such as information from higher eigenmodes, mode-mixing, and other non-linear phenomena in the tip-surface interaction. We present a new technique called General-mode (G-mode) where we capture the complete broad-band response of the cantilever at sampling rates of 1-100 MHz. The availability of the complete cantilever response facilitates the application of various physical models as well as multivariate statistical methods to extract information that has been unavailable from current SPM techniques. Polarization switching in ferroelectric and multiferroic materials underpins the next generation of electronic devices such as tunneling devices, field effect transistors, and race-track memories. The switching mechanisms in these materials are highly sensitive to the local defects and structural imperfections at the micro and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations necessitated the development of Piezoresponse Force Microscopy (PFM) imaging and spectroscopy techniques to measure and manipulate local polarization states. However, the current state-of-art PFM spectroscopy techniques suffer from serious compromises in the measurement rate, measurement area, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. Furthermore, these techniques only capture the narrow-band cantilever response. We report on a fundamentally new approach that combines the full cantilever response from G-mode with intelligent signal filtering techniques to directly measure material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. The improved measurement speed enables dense 2D maps of material response with minimal drift in the tip position.

This 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, U.S. Department of Energy.

8:40am **SP+AS+MI+NS+SS-MoM2 Development of Synchrotron X-ray Scanning Tunneling Microscopy***,* ***Nozomi Shirato,*** Center for Nanoscale Materials at Argonne National Laboratory*; H. Chang,* Ohio University*; M. Cummings,* Advanced Photon Source at Argonne National Laboratory*; S.W. Hla,* Center for Nanoscale Materials at Argonne National Laboratory*; V. Rose,* Advanced Photon Source at Argonne National Laboratory

Advancements of scanning probe microscopy have been contributing to broaden fundamental understating of surface physics. By combining high intense X-ray beam as a probe and a functionalized tip as a detector, synchrotron X-ray scanning tunneling microscopy has been developed in Advanced Photon Source at Argonne National Laboratory. The recent studies demonstrated the technique has capabilities to extract chemical information with sensitivity at the atomic limit [1] and localized magnetic contrast by utilizing polarized beams [2]. Furthermore, at Argonne, in order to fully exploit potentials of the microscope, a dedicated beamline is under construction. The soft X-ray beamline has the energy range of 400 to 1600 eV and is equipped with a polarizer and focusing optics. The capabilities of the beamline will benefit the communities to explore chemical, magnetic and electronic properties of materials at atomic resolution.

References

[1] N. Shirato et al., Nano Letters 14, 6499 (2014).

[2] A. DiLullo et al., J. Synchrotron Rad. 23, 574 (2016).

9:00am **SP+AS+MI+NS+SS-MoM3 Development and Integration of a Universal SPM head: Design Criteria and Challenges***, B. Guenther,* Sigma Surface Science GmbH, Germany*; J. Hilton,* Mantis Deposition*; A. Feltz,* Sigma Surface Science GmbH*;* ***Andreas Bettac,*** Sigma Surface Science GmbH, Germany

Recently we have developed an SPM microscope head that merges the needs for high resolution STM/QPlus[1]-AFM and at the same time satisfies the requirements for integration into different cryogen environments including tip and sample handling.

The new SPM head was integrated into different platforms, e.g. in a UHV Helium Flow Cryostat system for temperatures <10K and in a ^{3}He Magnet Cryostat UHV system for high magnetic fields (±12T) and temperatures <400mK.

This contribution focuses on design aspects and challenges for the new SPM head with respect to spatial restrictions, sample sizes/standards, QPlus and STM signal shielding as well as on first results (STM, STS and QPlus) obtained with the different instrumental setups.

[1] F. J. Giessibl, Applied Physics Letters 73 (1998) 3956

9:20am **SP+AS+MI+NS+SS-MoM4 How Soft Is a Protein? Stress-Strain Curve of Antibody Pentamers with 5 pN and 50 pm Resolutions***,* ***Alma Perrino*****[*]***,* Instituto de Ciencia de Materiales de Madrid, CSIC, c/ Sor Juana Ines de la Cruz 3, 28049 Madrid, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC,, Spain

Understanding the mechanical functionalities of complex biological systems requires the measurement of the mechanical compliance of their smallest components. Here, we develop a force microscopy method to quantify the softness of a single antibody pentamer by measuring the

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[*] **NSTD Student Award Finalist**

stress-strain curve with force and deformation resolutions, respectively, of 5 pN and 50 pm [1]. The curve shows three distinctive regions. For ultrasmall compressive forces (5-75 pN), the protein's central region shows that the strain and stress are proportional (elastic regime). This region has an average Young modulus of 2.5 MPa. For forces between 80 and 220 pN, the stress is roughly proportional to the strain with a Young modulus of 9 MPa. Higher forces lead to irreversible deformations (plastic regime). Full elastic recovery could reach deformations amounting 40% of the protein height. The existence of two different elastic regions is explained in terms of the structure of the antibody central region. The stress-strain curve explains the capability of the antibody to sustain multiple collisions without any loss of biological functionality.

[1] Alma P. Perrino and R.Garcia. How soft is a protein? Stress-Strain curve of antibody pentamers with 5 pN and 50 pm resolutions. *Nanoscale,* 10.1039/C5NR07957H (2016)

9:40am **SP+AS+MI+NS+SS-MoM5 AVS Medard W. Welch Award Talk: Action Spectroscopy: Characterizing Molecules at Surfaces and its Dynamics***, **Maki Kawai**[*],* Institute for Molecular Science, Japan*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; K. Motobayashi,* Nagoya Institute of Technology, Japan*; H. Ueba,* Toyama University, Japan **INVITED**

STM is a useful tool for spectroscopy utilizing its ultimate spatial resolution. Electronic and vibrational information that STS and inelastic electron tunneling spectroscopy (IETS) carries is not only the reflection of the static spectroscopic information but also related to dynamical phenomena as motion or reaction of molecules induced by the excitation of molecular states. Action spectroscopy is the method to related the action of molecules induced and is utilized to identify the quantum states of the molecules. Dynamical information includes as how molecular vibrations can couple with the relevant dynamical processes [1,2]. I will present typical eamples of how the fundamental excitation of vibration modes is coupled with chemical reactions at surfaces.

References:

[1] Y. Kim, K. Motobayashi, T. Frederiksen, H. Ueba and Maki Kawai, Profress in Surface Science 90 (2015) 85-143, and the references within.

[2] K. Motobayashi, Y. Kim, M. Ohara, H. Ueba and Maki Kawai, Surf. Sci. 634 (2016) 18-22.

10:40am **SP+AS+MI+NS+SS-MoM8 Near-Field Spectroscopy and Imaging of Single Nanoparticles***, **Yohannes Abate**, D. Seidlitz, A. Fali, S. Gamage, V.E. Babicheva, V.S. Yakovlev, M.I. Stockman,* Georgia State University*; R. Collazo, D. Alden,* North Carolina State University*; N. Deitz,* Georgia State University **INVITED**

We investigate nanoscale phase separation on single InGaN QDs and nanostructures by using high-resolution s-SNIN (scattering type scanning near-field infrared nanoscopy) technique in the mid-IR spectral region. We fabricated patterned nanolayers down to few atomic layers thick that allow determination of the near-field infrared response of InGaN/InN/GaN heterostructures quantitatively. We first calibrate the near-field IR amplitude contrast as a function of composition and thickness of the semiconductor nanolayers and QDs. We then use this quantitative leads to identify phase separation in single QDs. An advanced theoretical model is developed to guide the experimental results. Unlike previous models that consider the probe conical tip as approximate point dipoles or spheroids, our model considers the full geometry of the tip and all the sample and substrate layers.

11:20am **SP+AS+MI+NS+SS-MoM10 Atomically-resolved Three-dimensional Structures of Electrolyte Aqueous Solutions near a Solid Surface***, **Daniel Martin-Jimenez**, E. Chacon,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; P. Tarazona,* IFIMAC Condensed Matter Physics Center, UAM, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

Atomic-resolution three-dimensional images of electrolyte solutions near a mica surface demonstrate the existence of three types of interfacial structures [1-3]. At low concentrations (0.01-1 M), cations are adsorbed onto the mica until charge neutrality is reached. The cation layer is topped by a few hydration layers while anions are excluded from the mica surface [4]. At higher concentrations, the interfacial layer extends several nanometers into the liquid. It involves the alternation of cation and anion planes. Classical Fluid Density Functional calculations show that water molecules are a critical factor for stabilizing the structure of the ordered interfacial layer. The interfacial layer compatibilizes a crystal-like structure with liquid-like ion and solvent mobilities. At saturation, some ions precipitate and small ionic crystals are formed on the mica. The three-dimensional images have been acquired at 300 K.

[1] E. T. Herruzo, H. Asakawa, T. Fukuma, and R. Garcia, *Nanoscale* **5**, 2678-2685 (2013).

[2] K. Kobayashi *et al.The Journal of Chemical Physics* **138**, 184704 (2013)

[3] T. Fukuma *et al.Physical Review B* **92**, 7 (2015).

[4] M. Ricci, P. Spijker and K. Voitchovsky *Nat. Commun.* **5**, 4400 (2014).

11:40am **SP+AS+MI+NS+SS-MoM11 Super-resolution Optical and Chemical Imaging of Organic Thin Films using Tip-enhanced Near-Field Optical Microscopy***, A.L. Heilman, R. Hermann, **Michael Gordon**,* University of California at Santa Barbara

Sub-diffraction-limited (super-resolution) optical and chemical characterization of organic surfaces using a custom-built tip-enhanced near-field optical microscope with side-on and attenuated total reflectance (ATR) excitation and collection will be discussed. ATR illumination is combined with an Au optical antenna tip to show that (i) the tip can quantitatively transduce the optical near-field (evanescent waves) above the surface by scattering photons into the far-field, (ii) the ATR geometry enables excitation and characterization of surface plasmon polaritons (SPPs), whose associated optical fields can enhance Raman scattering from coumarin-6 (C6) and copper phthalocyanine (CuPc) films, and (iii) SPPs can be used to plasmonically excite the tip for super-resolution chemical imaging of patterned C6 and CuPc via tip-enhanced Raman spectroscopy (TERS). ATR-illumination TERS is quantitatively compared with the more conventional side-on illumination scheme using both experiment and FDTD optical simulations. In both cases, spatial resolution was better than 40 nm and tip on/tip off Raman enhancement factors were >6500. ATR illumination was shown to provide similar Raman signal levels at lower 'effective' pump powers due to additional optical energy delivered by SPPs to the active region in the tip-surface gap. Additional observations, such as the distance scaling of Raman enhancement and inelastic scattering generated by the plasmonic tip, as well as tip-enhanced photoluminescence imaging of patterned phthalocyanine films at spatial resolutions better than 20-30 nm, will be presented.

Surface Science
Room 104E - Session SS+AS+HC-MoM

Mechanistic Insights on Surface Reactions in Catalysis and at Novel Interfaces

Moderator: Bruce D. Kay, Pacific Northwest National Laboratory

8:20am **SS+AS+HC-MoM1 Study of Metal-Organic Complexation at Metal and Metal Oxide Surfaces by HREELS***, **Miao Wang**, C. Williams, S.L. Tait,* Indiana University

The ordering of organic molecules at surfaces and the formation of ordered metal nanostructures at surfaces have been extensively studied for the advancement of organic photovoltaics, nanoscale molecular electronics, and catalysts. There are many chemical systems that benefit from the combination of organic ligands with single-site metal centers to design and tune specific chemistries, but metal-organic complexation at surfaces has not yet been significantly studied. Molecular ligands on a surface with specific binding pockets can bind metal centers to achieve uniform oxidation states, as has been shown in prior studies by our group and by other groups. The goal of these studies is to improve selectivity in heterogeneous catalysts and to develop other novel surface chemistries. With that end in mind, we present new experiments with metal-organic coordination on oxide support surfaces. Most of the metal-organic surfaces studies have been done on metal surfaces to facilitate surface analysis. We have studied the redox assembly of 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ) and Pt on oxide surfaces, including rutile $TiO_2(110)$ using High Resolution Electron Energy Loss Spectroscopy (HREELS), Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). HREELS characterizes vibrational modes, which can provide key information about adsorbate interactions and metal-organic interactions at surfaces. DPTZ and Pt were sublimated onto the surface from a Knudsen-type evaporator. Submonolayer DPTZ vibrational modes were observed on Ag(111) (C-H bending modes at 400 cm^{-1}, 618 cm^{-1} and 772 cm^{-1}; ring deformation modes at 966 cm^{-1}, 1145 cm^{-1} and 1354 cm^{-1}) and on $TiO_2(110)$ (a ring deformation mode at 1580 cm^{-1} and a C-H stretching mode at 3060 cm^{-1}).

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[*] **Medard W. Welch Award Winner**

To see the vibrational modes of adsorbates on TiO_2, a Fourier deconvolution technique was applied to remove multiple excitations of surface phonon. Annealing DPTZ on Ag(111) at 170 °C caused significant changes to the HREEL spectra (C-H bending modes at 400 cm^{-1} and 740 cm^{-1}, ring deformation modes at 1100 cm^{-1}, 1445 cm^{-1}, 1574 cm^{-1}, a C-H stretching mode at 3080 cm^{-1}), but no observable changes were seen for DPTZ on TiO_2(110) until the sample was annealed at 290 °C. Adding equimolar Pt onto submonolayer DPTZ on Ag(111) caused similar vibrational changes to be observed, but at a lower temperature of 140 °C. HREELS studies of the Pt-DPTZ complex on TiO_2(110), Au(100), and other surfaces are ongoing. By studying the redox assembly of metal-organic complexes on these surfaces, strategies can be developed to customize and tune the reactivity of novel surface catalysts.

8:40am **SS+AS+HC-MoM2 Studies of Single-site Catalysts on Powdered Oxide Support through Redox Assembly***, **Linxiao Chen**, J.P. McCann, S.L. Tait,* Indiana University

High levels of reaction selectivity for selective alkane functionalization are generally difficult to achieve with metal nanoparticle heterogeneous catalysts, due to the variety of metal biding sites available. Motivated by the desire towards the development of uniform single-site metal centers at surfaces, our group has been working on the redox assembly of metal-organic systems at surfaces. On a single crystal gold surface, electrons are transferred from platinum to the ligand 3,6-Di-2-pyridyl-1,2,4,5-tetrazine (DPTZ). Utilizing this unique redox chemistry, long-range ordered 1D chains with an alternating metal-ligand structure were assembled at deposition of DPTZ with pre-adsorbed metallic platinum. All platinum sites are oxidized into Pt(II), and stabilized in the binding pocket between two DPTZ with identical chemical environment. Here, aiming at practical applications in catalysis, a novel solution-phase synthetic strategy was developed based on wet impregnation approach, in attempt to reproduce the similar metal-ligand structure on high-surface-area powdered oxide catalyst supports. X-ray photoelectron spectroscopy verified that the redox chemistry is applicable to real supports, and is crucial in the successful deposition of DPTZ despite a weak ligand-support interaction. The surface structure is further elucidated by X-ray diffraction and surface titration. It was concluded that the mobility of the metal and ligand on a rough support surface, and the existence of residual Cl from Pt precursors represent major challenges. This metal-ligand structure can be manipulated by tuning strength of interaction between the supports, metal and ligand. Initial catalytic tests with the methane oxidation reaction exhibited C-H activation ability and selectivity similar to traditional highly-dispersed Pt catalysts. We have compared these catalysts and explored the limitations of single-site metal-organic complexes at oxide supports. Though being significantly stabilized by the favored coordination geometry and the redox chemistry, the thermal stability of the metal-ligand structure needs to be further enhanced.

9:00am **SS+AS+HC-MoM3 Controlled Reactions of Coordination Complexes on Oxide Surfaces***, **Susannah Scott**,* University of California at Santa Barbara **INVITED**

The reactions of coordination complexes with functional groups on oxide surfaces (acidic and basic hydroxyl groups, Lewis acidic cations and Lewis basic oxide anions) can lead to anchored metal complexes with a high degree of uniformity when conducted under carefully controlled conditions (low-to-moderate temperatures, absence of moisture and/or O_2). Detailed characterization of these sites using spectroscopic methods, elemental analysis and reactivity studies leads to information about their structure and insight into the underlying structure of the oxide surface. Experiments with gold and silver complexes such as Me_2Au(acac) and Ag(acac) reveal that interactions with surface hydroxyls involving strong H-bonding to ligand donor atoms are primarily responsible for their dispersion as isolated metal sites. By modulating the hydroxyl density via thermal pretreatment, it is possible to control not only the surface density of metal atoms, but also their subsequent mobility. In the case of nucleation and subsequent autocatalytic growth of metal nanoparticles, it is possible to exert control over particle size via the initial metal complex-oxide surface interaction.

9:40am **SS+AS+HC-MoM5 Adsorption and Activation of CO_2 on Cu(997) at Low Temperature***, **Jun Yoshinobu**,* The University of Tokyo, Japan

Adsorption and activation of carbon dioxide on Cu(997) were investigated by infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). CO_2 molecules are *physisorbed* on Cu(997) at temperatures below 70 K. However, the vibrational spectra of adsorbed CO_2 depend significantly on the substrate temperature; IR spectra of CO_2 vibrational modes at 70 K show asymmetric Fano line shapes. On the other hand, at 85 K, the dissociation of CO_2 into CO was observed on Cu(997) by IRAS and XPS, but not on Cu(111). In addition, the reaction of CO_2 on Cu(997) surface at 340 K under CO_2 gas pressure of 0.8 mbar was investigated by ambient pressure XPS. A main reaction product on the surface was identified as carbonate (CO_3), based on estimation of the composition ratio of oxygen to carbon. CO_3 was produced on the surface through the reaction of CO_2 with atomic oxygen formed from CO_2 dissociation.

10:00am **SS+AS+HC-MoM6 D_2O Interaction with Planar ZnO(0001) Bilayer Supported on Au(111): Structures, Energetics and Influence of Hydroxyls***, **Xingyi Deng**, D.C. Sorescu, J. Lee,* National Energy Technology Laboratory

Ultrathin oxides with single or few atomic layers are considered new types of due to the emergence of film-specific structures with properties distinct from their bulk counterparts. ZnO(0001) bilayer grown on Au(111) adopts a planar, graphite-like structure via an intralayer relaxation from the bulk wurtzite structure. In this work, we investigate the interaction between D_2O and the planar ZnO(0001) bilayer grown on Au(111) with temperature programed desorption (TPD), low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. D_2O molecules adsorbed on this planar surface form two ordered overlayers, a (3 × 3) and a $(\sqrt{3} \times \sqrt{3})R30^\circ$, not seen before on any of the bulk ZnO single crystal surfaces. The apparent activation energies of desorption (E_d) estimated from TPD peaks agree well with the adsorption energy values calculated from DFT. The DFT calculations also reveal that both overlayers are mediated by extensive hydrogen bonding among the molecules but with different packing densities. The hydroxyl groups, accumulating very slowly on the ZnO(0001) bilayer surface under the standard ultrahigh vacuum (UHV) environment, strongly suppress the formation of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer but have less impact on the (3 × 3) overlayer. We suggest that the difference in packing densities of the overlayers leads to these findings such that only the (3 × 3) overlayer with a more open structure can accommodate small amounts of the adsorbed hydroxyls.

10:40am **SS+AS+HC-MoM8 Nanoscale Silicon as a Catalyst for Graphene Growth: Mechanistic Insight from In-Situ Raman Spectroscopy***, **Keith Share**, R.E. Carter,* Vanderbilt University*; P. Nikolaev, D. Hooper,* Air Force Research Laboratory*; L. Oakes, A.P. Cohn,* Vanderbilt University*; R. Rao,* Air Force Research Laboratory*; A.A. Puretzky,* Oak Ridge National Lab*; D.B. Geohegan, B. Maruyama,* Air Force Research Laboratory*; C.L. Pint,* Vanderbilt University

Nanoscale carbons are typically synthesized by thermal decomposition of a hydrocarbon at the surface of a metal catalyst. Whereas the use of silicon as an alternative to metal catalyst could unlock new techniques to seamlessly couple carbon nanostructures and semiconductor materials, stable carbide formation in bulk silicon prevents the precipitation and growth of graphitic structures. Here, we provide evidence supported by comprehensive *in-situ* Raman experiments that indicates nanoscale grains of silicon in porous silicon (PSi) scaffolds act as catalysts for hydrocarbon decomposition and growth of few-layered graphene at temperatures as low as 700 K. Self-limiting growth kinetics of graphene with activation energies measured between 0.32 – 0.37 eV elucidates the formation of highly reactive surface-bound Si radicals that aid in the decomposition of hydrocarbons. Nucleation and growth of graphitic layers on PSi exhibits striking similarity to catalytic growth on nickel surfaces, involving temperature dependent surface and subsurface diffusion of carbon. This work elucidates how the nanoscale properties of silicon can be exploited to yield catalytic properties distinguished from bulk silicon, opening an important avenue to engineer catalytic interfaces combining the two most technologically-important materials for modern applications – silicon and nanoscale carbons.

11:00am **SS+AS+HC-MoM9 Functionalization of Graphene on Ru(0001) with Atomic Oxygen***, **Zbynek Novotny**,* Pacific Northwest National Laboratory*; F.P. Netzer,* Karl-Franzens University, Austria*; Z. Dohnálek,* Pacific Northwest National Laboratory

Well-defined, monodispersed catalysts supported on oxidized carbon nanotubes are a promising class of new materials for heterogeneous catalysis. While such systems exhibit lower complexity compared to traditional catalysts, many questions, such as the reproducible preparation of carbon nanotubes and the range of functionalities used for anchoring of the clusters, make determination of their oxidation state and structure difficult. An analogous model system, graphene, can be prepared and studied under UHV conditions with great control. We employ scanning tunneling microscopy (STM) to study chemical functionalization of supported graphene on Ru(0001) with atomic oxygen. On Ru(0001) graphene forms a defect-free moiré structure with a periodicity of 3 nm, offering variety of distinct, regularly-spaced adsorption sites. Three different regions can be distinguished in STM images: bright regions (C atop of Ru) with the largest distance to the underlying Ru metal, dark hcp regions where graphene is closest to the metal, and medium-bright fcc regions where graphene is slightly further away compared to the hcp regions. Interestingly, for temperatures above 114 K, atomic oxygen (AO) is preferentially observed within the medium-bright fcc regions but in a minority of cases also in the hcp regions. The onset of AO mobility is observed at 400 K, where AO is occasionally moving inside the fcc region, or away from the less-stable hcp region towards the bordering fcc region. At higher temperatures (450-500 K), a dramatic increase in AO diffusion is observed allowing for AO transport between neighboring fcc regions through the hcp region. Upon encounter, the AO groups form stable immobile dimers and large clusters. The high-resolution time-lapsed data is used to assign the AO adsorption configuration to the on-top bonded enolate groups rather than the expected bridge-bonded epoxys. Our ongoing effort focuses on quantifying the enolate diffusion barrier and understanding their interactions with adsorbates such as H_2O, CO, and CO_2. The high thermal stability of enolate groups, and their large periodic separation (~3 nm) makes functionalized graphene/Ru(0001) an ideal model system for model studies of monodispersed catalysts.

11:20am **SS+AS+HC-MoM10 Interaction of BaO with H_2O, CO_2 and NO_2 Studied with APXPS and NEXAFS**, ***Osman Karslioglu***, *I. Zegkinoglou, L. Trotochaud, H. Bluhm,* Lawrence Berkeley National Laboratory

Barium is a constituent of several technologically important materials such as NO_x storage and reduction (NSR) catalysts in automobiles, getters for UHV applications, perovskite catalysts for electrochemical reactions and high-temperature superconductors. Interaction of barium compounds with simple molecules such as H_2O, CO_2 and NO_2 is thus of practical importance. We studied the interaction of in-situ prepared BaO with H_2O, CO_2 and NO_2 as a function of temperature and pressure using ambient pressure X-ray photoelectron spectroscopy (APXPS) and near-edge X-ray absorption fine structure (NEXAFS). Using in-situ preparation proved essential for preparing clean BaO, as the compound is extremely reactive even with minute amounts of H_2O and CO_2. We report the first experimental O K-edge X-ray absorption spectrum of clean BaO, for which the published spectra in the literature are more consistent with $BaCO_3$.

Applied Surface Science
Room 101B - Session AS+BI-MoA

Practical Surface Analysis I: Advancing Biological Surface Analysis/Imaging Beyond 'Show and Tell'

Moderators: Ian S. Gilmore, National Physical Laboratory, UK, Jordan Lerach, The Pennsylvania State University

1:40pm **AS+BI-MoA1 A Multi-technique Approach for Studying the Effect of Protein G B1 Orientation on Antibody Binding***, **Elisa Harrison**, G. Interlandi, D.G. Castner,* University of Washington

The orientation of adsorbed proteins on surfaces plays a vital role in the function and performance of biomaterials. Development of diagnostic tools such as sandwich ELISAs have focused on controlling the orientation of each protein layer. A full understanding of adsorbed proteins on surfaces, especially at the molecular level, is therefore essential. Our research addresses the challenges for characterizing protein orientation by developing new methods to study multilayer protein systems.

The aims of this study were to control and characterize the orientation of protein G B1, an IgG antibody-binding domain of protein G, on well-defined surfaces and measure the effect of its orientation on antibody binding using a variety of surface-sensitive tools and simulations. We hypothesize that binding selectivity would increase for well-ordered protein films due to higher availability of binding domains.

The surface sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS) enables us to distinguish between different proteins and their orientation by monitoring the changes in intensity of amino acid mass fragments. We have developed ToF-SIMS methods for analyzing the orientation of five different cysteine mutants of protein G B1 covalently attached to a maleimide surface. This technique was further extended by studying multilayer protein systems, specifically the binding of IgG antibodies to the protein G B1 films.

To study the effect of protein orientation on antibody binding, we utilized self-assembled monolayers (SAMs) to form protein G B1 films with both random and well-defined orientations. Using complementary techniques, such as X-ray photoelectron spectroscopy and quartz crystal microbalance with dissipation monitoring (QCMD), the ratio of bound IgG antibodies to protein G B1 increased from 0.06, when chemisorbed onto bare gold, to 0.2, when covalently attached to the surface. Further analysis revealed structure/orientation rearrangement of protein G B1 upon adsorption onto bare gold, which is likely responsible for decreased antibody binding.

Additionally, we developed and applied Monte Carlo (MC) simulations to predict protein orientation on a surface. The MC simulations showed that the outermost b-sheet of protein G B1 interacts most frequently with a hydrophobic surface. The predicted orientations were verified using molecular dynamics simulations, QCMD, and sum frequency generation.

The model systems explored in this study are a first step in developing methodology using state-of-the-art tools that can be applied to more complex systems and expand our knowledge and control of biomolecules on surfaces.

2:00pm **AS+BI-MoA2 ME-SIMS Revisited: Attempting to Unlock the Potential using Advancements in Sample Preparation and SIMS Technology***, **Nina Ogrinc Potocnik**,* Maastricht University, The Netherlands*; C.R. Anderton, L. Pasa-Tolic,* Pacific Northwest National Laboratory*; R.M.A. Heeren,* Maastricht University, The Netherlands

This year marks the 20th anniversary of Wu and Odom first describing the application of a solid organic matrix to improve the ionization efficiency of molecular species in secondary ion mass spectrometry (SIMS) measurements. This so-called matrix enhanced-SIMS (or ME-SIMS) method overcame one of the disadvantages of SIMS analysis, providing the capability of imaging large molecules with high spatial resolution. With increased ionization efficiency and minimized fragmentation caused by the primary ion beam, the method is ideal for detection of intact bimolecular species, where detection of proteins greater than 10,000 Da is feasible. However, the combination of instrumentation limitations of resolving isobaric compounds and lateral diffusion caused by matrix application has pushed this technique into near irreverence. Here, we reevaluate ME-SIMS with new technologies such as parallel MS/MS capabilities on the PHI nano-TOF TRIFT V, and the custom-build FTICR-SIMS capable of unmatched mass resolving power and mass accuracy. We also explore new matrix application techniques to revisit the potential of ME-SIMS and apply it to a number of different biological settings.

Specifically, we reexamined peptide standard profiling with the addition of tandem MS on the nano-TOF TRIFT V . The ability to isolate precursor ions with a 1 Da mass window, followed by a high-energy collision-induced dissociation (CID), enables a very precise fragmentation of molecules. We observe peptide fragmentation through the amino terminus, a_m, providing us with a specific fragmentation pattern for identification of peptide species and opening doors to *de novo* peptide sequencing. Further on, we applied it for characterizing tryptically digested peptides investigating the applicability to bottom-up proteomics. We then imaged model plant and mammalian tissue sections that were subjected to a variety of different matrices *via* supplication using a home-built sublimation chamber. Matrix sublimation produces small, homogenous crystal sizes, without the need for solvents that delocalize molecular species. Consecutive sections were analyzed by FTICR-SIMS, to accurately identify molecular species of interest, and by the nano-TOF TRIFT V for high lateral resolution images and confident identification of said species with tandem MS.

2:20pm **AS+BI-MoA3 Improvements in SIMS Methods and Instrumentation in Effort to Make Measurements Biologists Can Use***, **Christopher R. Anderton,*** Pacific Northwest National Laboratory **INVITED**

The ability of mass spectrometry imaging (MSI) to visualize chemical distributions within samples has made it an increasing popular method in many biological fields, including medicine, pathology, and microbial ecology. Secondary ion mass spectrometry (SIMS) is a surface sensitive MSI technique that offers extensive versatility in its ionization and analysis modes, requires relatively minimal preparation, and can achieve the highest lateral resolution of any MSI method. Early bio-applications of SIMS routinely focused on pursuing the molecular information attainable by softer ionization methods (e.g., matrix assisted laser desorption/ionization), but with the added benefit of achieving subcellular lateral resolution. Even though primary ion beams used in SIMS measurements afford smaller probing areas than other ionization methods, their excessive energy typically causes extensive fragmentation of most biorevelent molecules. This renders identification of parent molecules from the detected secondary ions a nontrivial endeavor. Nevertheless, recent improvements in SIMS instrumentation, methods, and data analysis approaches have unlocked biochemical information that was previously unattainable. Here, I will discuss our efforts in improvements in sample preparation methods and the employment of unique mass spectrometer technology for analyzing biological material. Stable isotope probes were used to decode lipid distributions within model and cellular membranes, to reveal the intercellular delivery of drug-loaded polymeric nanoparticles, and to elucidate metabolic processes of phototrophic communities. The use of Fourier transform-based mass spectrometers, which have unparalleled mass accuracy and mass resolving power, and tandem mass spectrometry methods have allowed us to unravel the extreme spectral complexity of biological SIMS measurements, while increasing the confidence in our measurements. Lastly, we have revisited previously reported sample preparation routes that were never fully adapted by the SIMS community, in part because they were shackled by the limited ability of more commonly employed mass analyzers.

3:00pm **AS+BI-MoA5 Towards Bacterial Differentiation with Quantitative SIMS***, **Christopher Szakal**, S. Da Silva,* National Institute of Standards and Technology (NIST)*; N. Olson,* National Institute of Standards and Technology(NIST)

Large geometry secondary ion mass spectrometry (LG-SIMS) has been used extensively for particle analyses and geochemical analyses, owing to its ability to maintain adequate mass resolution while operating at high secondary ion transmission. Efforts will be presented that extend the knowledge acquired in these application areas to single bacterial cell analyses of elemental species. To be useful, LG-SIMS results need to be quantitative for the amounts of a given element per cell and/or in ratios of different elements within each cell. Approaching this level of detail requires the establishment of the natural variability of such data from cell-to-cell, the reproducibility of the measurement technique, and whether the data is relevant to pertinent questions about the cellular population. Progress will be shown towards achieving these aims for single bacterial cells within different known growth conditions, including analytical figures of merit for LG-SIMS elemental ratios. Prospective application areas will be presented, along with potential pitfalls of such an approach.

3:20pm **AS+BI-MoA6 New Insights into the Microenvironment of Cancerous Tissue by Combined Mass Spectrometry, Microscopy and Multivariate Analysis*, Tina Angerer,*** University of Gothenburg, Sweden*; Y. Magnusson, G. Landberg,* Sahlgrenska Cancer Center, Sweden*; J.S. Fletcher,* University of Gothenburg, Sweden

Introduction

Mass spectrometric imaging is of growing interest for the medical field, both in applied and basic research[1]. Particularly, imaging secondary ion mass spectrometry (SIMS) is becoming of increasing value to clinicians and has been used on a number of tissues samples to successfully identify and localize different chemical components to various areas of the tissue and answer disease related questions[2]. Fatty Acid Synthase (FAS) has been shown to be increased in many cancer types and is of growing interest as therapeutic target[3]. The changed lipid composition due to increased FAS activity is an ideal ToF-SIMS study target.

Methods

With the J105- *3D Chemical Imager* (Ionoptika Ltd), fitted with a 40 kV gas cluster ion gun[4], we are now able to overcome some previous limitations of ToF-SIMS analysis and image large intact molecular species at high spatial and high mass resolution simultaneously. To capitalize on these improved capabilities we performed imaging SIMS on fresh frozen hydrated and freeze dried, ductal mammary breast cancer sections, followed by H&E staining of the analysed sections.

Results

SIMS enables us to distinguish between different areas of the diseased tissue. Multivariate analysis facilitates localizing and grouping the up to 10,000 different signals generated from the tissue to produce comprehensive chemical profiles assigned to different areas in the tissue revealing underlying structures. We have identified a number of molecules which can be, due to high spatial resolution, clearly assigned to the cancerous regions, characterized by conventional histological staining, in different breast cancer sections. Additionally, studying the distribution of specific single ions reveals reoccurring patterns of changes and gradients within the cancerous areas which cannot be observed in the conventionally stained image. Therefore ToF-SIMS can provide deeper insights into tumor metabolism and progression. Our results agree with findings from experiments using different methods, which confirm these molecules to be cancer markers while more importantly elucidating new information form the tissue with cellular resolution.

Conclusions

Imaging ToF-SIMS is a valuable tool for cancer research and can provide new insights into chemical changes within tumors. Further application of ToF-SIMS imaging will be used to study different modes of disease progression and treatment response.

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4:00pm **AS+BI-MoA8 Super-resolution Mass Spectrometry Imaging of Biological Materials with the New 3D nanoSIMS*, Ian S. Gilmore*,** *M.K. Passarelli,* National Physical Laboratory, UK*; A. Pirkl, R. Moellers, E. Niehuis,* ION-TOF GmbH, Germany*; A.A. Makarov,* Thermo Fisher Scientific*; H.F. Arlinghaus,* ION-TOF GmbH, Germany*; R. Havelund, P.D. Rakowska, A.M. Race, A.G. Shard,* National Physical Laboratory, UK*; A. West,* GlaxoSmithKline*; S. Horning,* Thermo Fisher Scientific*; P. Marshall,* GlaxoSmithKline*; M.R. Alexander,* The University of Nottingham, UK*; C.T. Dollery,* GlaxoSmithKline

SIMS has become an important technique for the surface analysis of biological materials. However, critical challenges have hampered the uptake into the life-science industry and biomedical discovery. To succeed in this important sector, it has to progress beyond "Show and Tell". Biological samples have complex chemistry and an extraordinarily large dynamic range of concentration. The present state-of-the-art struggles to identify unknowns owing to insufficient mass resolving power and mass accuracy of time-of-flight analysers. The situation is further complicated by sample form and vacuum compatibility.

To address this issue, we have developed a powerful new hybrid SIMS instrument combining an Orbitrap™-based Thermo Scientific™ Q Exactive™ HF instrument and a dedicated ToF-SIMS 5. The instrument is equipped with high-resolution ion beams including a new micron resolution argon cluster ion beam for biomolecular imaging and 3D analysis of organics and an ultra-high resolution Bi cluster focussed ion beam with < 80 nm resolution. The ToF analyser allows high-speed imaging needed for 3D analysis and the High Field Orbitrap analyser allows high mass resolution, mass accuracy and MS/MS for chemical identification. The instrument is designed for life-sciences applications including sub-cellular 3D imaging of metabolites, imaging of bacteria and biofilms and imaging of medical devices with complex topographies that confound traditional instrument designs.

We show data demonstrating the unique advantages of this novel instrument. Imaging with large argon clusters provides rich biomolecular spectra including intact lipids and metabolites. Existing state-of-the-art instruments are limited to a mass resolving power of around 6,000 which is insufficient to allow unique identification. We show images of mouse brain with a sub-cellular spatial resolution of less than 2 microns simultaneously with a mass resolving power of over 100,000 for intact lipids. We fully separate the (3'-sulfo)Gal-Cer(d18:1/24:1(2-OH)) and (3'-sulfo)Gal-Cer(d18:1/25:0) sulfatides, which reveals a difference in spatial distribution. In the low mass region, mass resolving powers of >400,000 are achieved allowing clear separation of the low abundance metabolite dopamine from other peaks. We show the ability to image the drug amiodarone with sub-cellular resolution and show that the mass spectra are not affected by sample topography. The instrument is also equipped with state-of-the-art cryogenic sample preparation specifically designed for high-resolution biological imaging.

All animal studies were ethically reviewed and carried out in accordance with Animals (Scientific Procedures) Act 1986

4:20pm **AS+BI-MoA9 High-resolution, Sub-cellular Imaging of Pharmaceutical Localization by Correlative SIMS and TEM*, Paulina Rakowska,*** National Physical Laboratory, UK*; H. Jiang,* University of Western Australia*; I.S. Gilmore,* National Physical Laboratory, UK

To accurately predict the pharmacological effect of potential drug candidates, there is a strong need in the pharmaceutical industry to image the disposition of drugs at the sub-cellular level and even within specific organelles. This is needed to answer long-standing questions about whether drug concentrations are sufficiently high in the right places to have a therapeutic effect, or if the medicine is lodging within cellular components and causing toxicity. If anomalies were spotted earlier, it might help to explain toxicities or lack of efficacy of a medicine and reduce costly late-stage failures.

Mass spectrometry imaging techniques are well-suited to measure drug distribution in biological samples and have the advantage of label-free analysis. The CAMECA nanoSIMS (secondary ion mass spectrometry) can provide elemental images with high lateral resolution of 50 nm. These high-resolution ion images can be correlated to electron microscopy images. This combination of techniques provides very precise and detailed information of cell morphology, subcellular processes and localization of different molecules within the cells. However, these high-performance instruments require high vacuum and complex sample preparations. Therefore, the sample handling needs careful consideration. Biological samples can suffer from ultrastructural reorganization or the loss or translocation of molecules, which can occur with dehydration under high-vacuum conditions. Chemical fixation of the samples followed by embedding in resin are common in the studies of cell biology by TEM but the solvents used for sample dehydration have a severe effect, translocating or even removing the drug from the cell all together. This has been a fundamental barrier for the use of the technique for intracellular drug localization measurement.

We present a correlative nanoSIMS and TEM imaging of a highly lipophilic drug – amiodarone within lung macrophages dosed at therapeutic concentrations. The protocol used for the fixation and resin-embedding of the cells prevented the drug from being removed from the organelles during solvent treatment. We are able to show, with unprecedented detail, the drug accumulating in lysosome organelles.

4:40pm **AS+BI-MoA10 Sub-Micron Imaging and Identification of Molecular Chemistry by TOF-SIMS Parallel Imaging MS/MS*, Gregory Fisher*[*],** Physical Electronics*; N. Ogrinc Potocnik, A.L. Bruinen,* Maastricht University, The Netherlands*; J.S. Hammond, S.R. Bryan,* Physical Electronics*; R.M.A. Heeren,* Maastricht University*; S. Iida, T. Miyayama,* ULVAC-PHI **INVITED**

A recently introduced TOF-TOF imaging mass spectrometer allows conventional TOF-SIMS (MS^1) analysis and product ion (MS^2) analysis to be

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[*] **ASSD Peter Sherwood Award**

achieved simultaneously and in parallel. Secondary ions for MS^1 and MS^2 analysis are produced from the same area of the surface by a pulsed and digitally raster-scanned primary ion nanoprobe. The sensitivity of the parallel imaging MS/MS spectrometer is high so that the analytical ion dose may be minimized; therefore, precious and one-of-a-kind samples may be probed without significant damage or degradation. Fragmentation of the molecular precursor ions, defined by a 1 Da precursor selection window, is accomplished by collision-induced dissociation (CID) at 1.5 keV in an activation cell of Ar gas at high pressure. Lateral resolutions produced in both MS^1 and MS^2 images are demonstrated to be in the range of $100\text{ nm} < \Delta l_{80/20} < 1\ \mu\text{m}$. This tandem MS imaging capability has been brought to bear for straightforward identification as well as multifaceted studies involving biological, material, and polymer specimens. We will summarize here some of our ongoing biological research, revealing molecular identification at sub-micron practical lateral resolution.

One study concerns song bird ontogeny in male zebra finch (*T. guttata*). Several sulfatides, phospholipids, sterols and fatty acids have been identified as playing a role in song learning. We have employed parallel imaging MS/MS to unravel the roles of specific molecules because the shortcomings of TOF-SIMS imaging alone does not permit conclusive molecular identification and imaging. We have evidence suggesting that distinct sulfatides are active primarily within the song nuclei while cholesterol and specific fatty acids are active in signaling between the song nuclei.

In other work, we have probed the role of lipids and metabolites in disease states of zebrafish (*D. rerio*) that have been infected with *M. marinum*, a form of tuberculosis. The bacteria initiate a granulomatous inflammation, and first signs of the disease are observed in the spleen. We have observed so far that α-tocopherol is elevated in infected tissue as well as in the granuloma, but is not present in the necrotic cells. Cholesterol is elevated primarily in the granuloma. The role of phospholipids appears to differ, specific molecules being either elevated or depressed in the infected tissue. We have preliminary evidence of a metabolic source for bacterial growth. For example, we observe a phosphocholine, PC(16:0/16:0), to be elevated in the granuloma. However, in the necrotic cells surrounding the granuloma we observe elevated signals of a fatty acid, FA(16:0).

Plasma Science and Technology
Room 104D - Session PS+AS+SS-MoA

Plasma Surface Interactions

Moderator: Richard van de Sanden, FOM Institute DIFFER, Netherlands

1:40pm **PS+AS+SS-MoA1 Atomic-scale Analyses of Plasma Etching for Unconventional Materials in Microelectronics**, ***Satoshi Hamaguchi***, *K. Karahashi,* Osaka University, Japan **INVITED**

As the sizes of semiconductor devices continue to diminish and are now approaching atomic scales, the downsizing of transistors following Moore's law is bound to end in the near future. However, the continuing market demand for higher performance and lower energy consumption of large-scale integrated (LSI) circuits has driven invention of new device technologies such as three-dimensional (3D) device structures and devices based on non-silicon materials. Manufacturing of these non-conventional devices also poses new challenges for processing technologies. For example, magnetic materials used in magnetoresistive random-access memories (MRAMs) cannot be etched efficiently by the existing reactive ion etching (RIE) technologies, which has so far limited the level of integration of MRAM devices. The modern near-atomic-scale devices also require atomic level precision in their manufacturing processes, which has also driven new technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE). In this study, we shall review our recent work on analyses of etching selectivity and surface chemical reactions for magnetic materials [1,2] metal oxides[3,4], Si-based materials [4] as well as damage formation mechanisms [6,7] due to ion bombardment during RIE processes. In our analyses, we use multi-beam injection experiments [8] and molecular dynamics (MD) simulations to emulate elementary processes of plasma-surface interactions that take place in RIE processes.

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2:20pm **PS+AS+SS-MoA3 Plasma Wall Interactions: Y_2O_3 Wall Interaction in Cl_2 Plasma Etching of Si and NF_3 Plasma Cleaning**, ***Tianyu Ma***, *T. List, V.M. Donnelly,* University of Houston

The walls of a plasma etching chamber play a critical role in causing variability of processing metrics such as rate, profile shape and selectivity. Small changes in the nature of the chamber wall surfaces can affect radicals sticking coefficients, recombination probabilities, and other heterogeneous reactions that will cause changes in the number densities of species in the plasma, which in turn affects the process. Therefore, a stable chamber wall material is essential for plasma processes, and in particular plasma etching. Compared to traditional alumina and silica wall material, Y_2O_3 has high chemical stability and extending lifetime, making it one of the preferred wall materials in etching systems. Consequently, studies were performed in a chamber with Y_2O_3-coated walls to determine time-dependent variations in the number densities of species in inductively coupled Cl_2/Ar and NF_3/Ar plasmas. Si was etched in Cl_2 plasmas, after which, the wafer was removed and an NF_3 plasma was used to remove etching products that deposited on the walls. This etch-clean procedure was repeated many times, simulating an integrated circuit manufacturing etch process. Optical emission spectroscopy (OES) and Langmuir probe analysis were performed to characterize plasma. Y_2O_3-coated coupon pieces exposed to the plasma were examined by X-ray photoelectron spectroscopy (XPS). Number densities of Cl_2, Cl, O, and F were obtained with rare-gas actinometry during the entire etching and cleaning cycles. Emissions from Si, SiCl, $SiCl_2$, $SiCl_3$, SiF, and N_2 were also recorded. After exposure to the NF_3 plasma, Cl number densities are relatively low when no substrate bias is placed on the Si substrate. As soon as bias is initiated, Cl number density rises steeply at first and then slowly maximizes. This is attributed to then displacement of F on the walls with a $SiCl_x$ containing layer. Apparently Cl on its own cannot remove F efficiently, but the reaction of Si-containing etching products produces SiF surface species that desorb and are observed as transient SiF emission in the first moments of etching. Cl recombination on this surface is much lower than on the fluorinated Y_2O_3 surface. Once prepared by etching Si with bias, the Cl number density remains high if bias is extinguished and etching nearly stops. The higher recombination coefficient on fluorinated surfaces is attributed to the longer residence time of physisorbed Cl, caused by the attraction to positively charged Y sites that are created when Y forms mainly ionic bonds with F.

2:40pm **PS+AS+SS-MoA4 Novel atomic order CD Control Technology by Fusion of Quasi-ALE and ALD**, ***Yoshihide Kihara***, *T. Hisamatsu,* Tokyo Electron Miyagi Limited, Japan*; T. Oishi, S. Ogawa, H. Watanabe,* Tokyo Electron Miyagi Limited*; A. Tsuji, M. Honda,* Tokyo Electron Miyagi Limited, Japan

In the recent years continuous scaling has required the use of multiple mask patterning technologies such as double and quadruple patterning, and increasingly thin EUV mask films are being planned to be used in the near future. In the patterning process, the fabrication of multilayer films requires the precision of atomic layer level accuracy (within nm level). Some critical challenges that patterning schemes face includes thinning of mask materials, reduction of ARDE related CD-loading, and reduction of LER and LWR. This requires the realization of highly selective etch processes that can address the challenges without trade-offs in other process specifications.

One method to increase the mask selectivity to enable mask thinning, which is one of the major patterning issues, Si-ARC is etched in a depositing condition which protects the resist mask surface, utilizing the material difference between the mask material and the antireflective layer (Si-ARC). However, to enhance selectivity, extra amount of the deposition can be generated. The amount of deposition flux fluctuates depending on the pattern density, leading to CD loading. In order to solve the tradeoff between selectivity and loading, we have proposed a Quasi- Atomic Layer

Etching (Quasi-ALE) which is a modification of ALE to employ thin-film adsorption and activation by low ion energy [1]. In this paper, Quasi-ALE is applied to Si-ARC etch step to address three challenges; high selectivity, pattern-independent CD-loading, and vertical etch profiles.

We have also proposed the combination of ALD with etch as CD-loading-free CD control technique [2]. By combining ALD and Quasi-ALE, excellent CD controllability was achieved to address the entire patterning process issues without tradeoffs. In the presentation, various merits of the Fusion Process, which is a combination of Quasi-ALE and ALD, in patterning process, will be introduced. Fusion Process has a significant potential to solve critical challenges in the patterning process of N7, N5 and beyond.

Reference

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3:00pm **PS+AS+SS-MoA5 Development of a New Analysis Technique of Nanostructures Etched by Plasmas: Quasi In-Situ TEM EDX Characterization***, Matthieu Serege,* LTM, Univ. Grenoble Alpes, CEA-LETI*; G. Cunge,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; L. Vallier, E. Latu-Romain,* LTM, Univ. Grenoble Alpes, CEA-LETI*; O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

As the size of integrated circuit continues to shrink, plasma processes are more and more challenged and show limitations to etch nanometer size features in complex stacks of thin layers. The achievement of anisotropic etching relies on the formation of passivation layers on the sidewalls of the etched features which act like a protective film that prevents lateral etching by the plasma radicals. However, this layer also generate a slope in the etch profile and it's difficult to control the layer thickness. Another thin layer called "reactive layer" is also formed at the bottom of the feature where the energetic ion impact mix the material to be etched with the plasma radicals. Etch products are formed allowing a high etch rate of the silicon substrate. It starts to be realized that controlling the thickness of this reactive layer is the key to achieve very high selective processes. Indeed, accurate etch stop on an ultra-thin layer is only possible if the thickness of this stop layer is higher than the thickness of the reactive layer otherwise damages are created underneath the stop layer.

A better understanding of these layers chemical nature, thickness and deposition mechanism is mandatory, but the main problem is that the layers to be analyzed are chemically highly reactive because they contain large concentrations of halogens and they get immediately modified (oxidized) when exposed to ambient atmosphere.

In this work we develop an original, simple and extremely powerful approach to observe passivation layers quasi in-situ (i.e. without air exposure): After plasma etching, the wafer is transported *under vacuum* inside an adapted suitcase to a deposition chamber where it is encapsulated by a metallic layer (magnetron sputtering PVD). Then, the encapsulated features can be observed ex situ without chemical / thickness modification using FIB-SEM (specimen preparation) coupled with a TEM-EDX analysis: HRTEM observation provides an extremely precise measurement of the passivation layer and encapsulation morphology. In parallel, STEM-EDX is used to map the main atomic element in our specimen, supplying qualitative information on the layer chemical composition. STEM-EDX is also used in profile mode to give us more accurate quantitative analysis. We are able to estimate the (relative) quantitative atomic concentration along a line scan profile on the feature sidewalls.

The measurements relatively fast, provide accurate analysis at the nanoscale, and are highly promising to better understand plasma etching processes. Therefore, this technique will be very helpful to develop innovative processes controlled at the nanometer range.

3:20pm **PS+AS+SS-MoA6 Atomistic Simulations of He Plasma Modification of Si/SiN Thin-Films for Advanced Etch Processes***, Vahagn Martirosyan,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; E. Despiau-Pujo,* CNRS - LTM, France*; O. Joubert,* LTM, Univ. Grenoble Alpes, CEA-LETI, France

Due to high ion bombardment energies and significant fragmentation rates, conventional continuous

wave (CW) plasma processes are not able to selectively etch ultra-thin films without damaging the

active layers of advanced nanoelectronic devices (e.g. FDSOIs, FinFETs). In particular, silicon nitride

or low-k spacers etching must be performed with nanoscale-precision without creating defects to the

underlayer substrate, to preserve device performances and be compatible with epitaxial steps. To

solve this problem, one possible alternative is to use a recently developed etch technology, which

consists of two steps [1]. In the first step, the material to be etched is exposed to a hydrogen (H 2) or

helium (He) ICP or CCP plasma; in the second step, the modified material is chemically etched by wet

cleaning or exposure to gaseous reactants only.

Due to the complexity of plasma-material interactions, the development of such a new etch approach

requires a more detailed understanding of the fundamental mechanisms involved in the process.

Therefore, we develop Molecular Dynamics (MD) simulations to study the Si-He and Si-N- He systems

and provide an overview of the reaction processes at the atomic scale. The objective is to understand

precisely the role of ion energy in the self-limited ion implantation, and to determine the relationship

between the flux/energy of plasma species (He +) bombarding the surface and its structural/chemical

modifications.

In this work, we investigate the interaction between helium plasma species (He+ ions) and

silicon/silicon nitride via MD simulations, by studying the influence of ion energy (5-100eV) and ion

dose on the substrate modification. For He/Si interactions, simulations show an initial He implantation

followed by the formation of a stable modified layer at steady state, composed of two parts: a Si-He

mixed amorphous layer and a thin sublayer, which is crystalline but enriched in helium. According to

our results, the higher is the ion energy, the more rapid is the contamination and the thicker is the

amorphous layer. Few or no Si sputtering is observed for energies lower than 100eV, confirming that

He plasmas can modify/weaken the material on a precise depth without etching it. Amorphisation of

the material leads to the rupture of crystalline Si-Si bonds and to the creation of a less dense modified

layer, facilitating its subsequent removal by wet or dry etching. Mechanisms of helium

retention/desorption, as well as comparisons between He/Si and He/SiN interactions, will be

discussed during the presentation.

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4:20pm **PS+AS+SS-MoA9 Patterned Chromium Hard Mask Etching in a Two Reactant Gas for Bit Patterned Media Template Fabrication***, **Daniel Staaks**[*],* Molecular Foundry, Lawrence Berkeley National Lab*; X. Yang,* Seagate Technology*; S. Dallorto, S.D. Dhuey, S. Sassolini,* Molecular Foundry, Lawrence Berkeley National Lab*; K.Y. Lee,* Seagate Technology*; I.W. Rangelow,* Ilmenau University of Technology, Germany*; D.L. Olynick,* Molecular Foundry, Lawrence Berkeley National Lab

Plasma-based dry etching is one of the most important nanofabrication methods for transferring full-wafer patterns. As feature sizes approach the single digit nanometer regime, there is an urgent need to develop a comprehensive and detailed understanding of the associated etching mechanisms. Additionally, challenges in obtaining high anisotropy, high selectivity, and robust critical dimension control must be addressed.

Highly selective chromium etching masks are an area of particular interest. Chromium has a widespread utility in not only manufacturing photolithography masks, but also in fabricating high-resolution nanoimprint templates. For example, we use it as a highly selective hard

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[*] **Coburn & Winters Student Award Finalist**

mask when etching SiO2 to achieve Bit Patterned Media templates towards sub-5nm features (7Tb/in^2).

To date, there have been few investigations into patterned chromium films. The limited studies available involve micron-sized features and patterning by the erosion of polymer masks, which make extrapolation to the single-digit nano regime very difficult. In this work, we bridge the gap for nanoscale-patterned films. We etch a patterned 20nm layer of chromium in low pressure and low power Cl_2/O_2 plasmas. We investigate the profile evolution of features ranging from 15nm- to 200nm in pitch. Previous work in etching blanket chromium films revealed that chromium etch rate was influenced by substrate temperature and Cl_2/O_2 flow [1]. Here, we vary percent O_2 flow (1%, 50%, 87%) and temperature (-50°C, +20°C) to explore the effects on lateral etching mechanisms, etch lag, and anisotropy. Using a highly selective HSQ mask for etching the chromium allows us to better determine the involved etching mechanisms. High-resolution micrographs of thin film cross-sections show significantly enhanced anisotropy at low temperatures.

Additionally, the unique etching chemistry of chromium must be considered when evaluating the material as a mask. Most materials form multiple volatile binary compounds during the etching process. Chromium, on the other hand, forms a single ternary compound: chromyl chloride. This enables us to study the effect of two-reactant gas chemistry on the etched feature profile. Results indicate that gas phase transport and surface mass transport of oxygen and chlorine are influential to profile shapes. Moreover, the effective local oxygen concentration inside the trench is important, and surface-dominated reactions highly affect the profile. Chlorine rich and chlorine poor chemistries promote very different surface reactions.

[1] D. Staaks, et al., Low temperature dry etching of chromium towards control at sub-5 nm dimensions, Nanotechnology 2016, submitted manuscript

4:40pm **PS+AS+SS-MoA10 Alternative Solutions for Nanometric-Precision Etching: H2 Plasmas Modification of Si/ SiN Thin-Films**, ***Emilie Despiau-Pujo**, V. Martirosyan, O. Joubert,* LTM - CNRS/Univ Grenoble Alpes/CEA, France

Consisting of several ultrathin layered materials, advanced transistors (FDSOI, FinFET) must be etched with a nanometric precision and nearly infinite selectivity to preserve the electronic properties of active layers (e.g. the silicon channel), a challenge which cannot be addressed by conventional CW plasma processes. To achieve uniform and damage-free etching of multi-layered transistors, an alternative etch approach has been recently proposed, consisting in two steps. In a first step, the film to be etched is modified in volume by exposition to a hydrogen or helium conventional CCP or ICP; in a second step, the modified layer is selectively removed by wet cleaning or exposure to gaseous reactants only. Such a two-steps process showed promising results for silicon nitride spacers etching [1]. To assist the development of this new technique, Molecular Dynamics (MD) simulations - coupled to experiments - are used to investigate the interactions between H2 plasmas and Si/SiN films. These atomic-scale simulations aim at better understanding the relationship between the flux/energy of plasma species (Hx+ ions, H radicals) bombarding the surface and its structural/chemical modifications.

Although one material of interest is silicon nitride, the study of Si-H systems constitutes a first step to understand the impact of ion energy (5-100 eV) and ion dose on the substrate modification and self-limited ion implantation. Simulations of cumulative Hx+ (x=1-3) ion bombardment show a rapid hydrogenation of Si followed by the formation of a stable modified layer at steady state. This modified layer is composed of a thick amorphous Si-H mixed layer and a thin sublayer, quasi-crystalline but enriched in hydrogen. As hydrogen is highly chemically reactive, ion implantation leads to the rupture of crystalline Si-Si bonds and to the creation of SiH, SiH2, SiH3 covalent bonds in the modified material. At the bottom of the modified layer, hydrogen tends to saturate the dangling bonds of the amorphous silicon and to create SiH3 bonds, thus fracturing the substrate into a modified hydrogenated layer weakly bound to the underlying crystalline material (Smartcut-like mechanism). The influence of ion dose, ion energy and ion type on the modified layer thickness (and thus on the subsequent etch precision) are discussed. Comparisons between pure ion implantation and exposition to various H2 plasma conditions (simulated by bombarding the Si/SiN substrates with both Hx+ ions and H radicals) are also presented. [1] N. Posseme, O. Pollet, S. Barnola, Applied Physics Letters 105, 051605 (2014)

5:00pm **PS+AS+SS-MoA11 Plasma Dynamics at the Surface Interface in Low Pressure Capacitively and Inductively Coupled Plasmas**, ***Martin Blake**, D. O'Connell,* University of York, UK*; A.R. Gibson,* LPP, CNRS, Ecole Polytechnique, Université Paris-Saclay, France*; T. Gans,* University of York, UK

The plasma-surface interface in low temperature, low pressure plasmas used for industrial

wafer processing is difficult to characterise. However, understanding the plasma dynamics

at this interface is key for further optimisation of industrial plasma processes. Of particular

relevance are the densities of reactive species, such as atomic oxygen, in this region. In this

work a methodology has been developed based on newly augmented fast optical

techniques which can probe reactive species densities in the wafer region without the need

for expensive laser equipment. This technique, known as energy resolved actinometry

(ERA)[1], utilises phase resolved optical emission spectroscopy (PROES) measurements of the

direct and dissociative electron-impact excitation dynamics of three distinct emission lines,

750.4 nm (argon, added in small concentrations as a tracer gas) and 777.4 nm, 844.6 nm

(atomic oxygen). Through the ratio of the excitation functions and their energy dependence

we determine both the atomic oxygen density and the mean electron energy above the

electrode surface.

In this work ERA has been applied to measure atomic oxygen densities and local mean

electron energies in a low pressure (1 – 100 Pa) oxygen plasma produced in a GEC reference

cell system [2], operated at 13.56 MHz in both capacitive and inductive modes at power

inputs ranging from 50 – 500 W. Additional characterisation of the plasma-surface interface

is carried out through the use of a retarding field energy analyser (RFEA) to measure the ion

energy distribution at the surface. The combination of both approaches allows for

information on the neutral and ion dynamics in the surface region, both of which are known

to be important for process outcomes.

A two-dimensional hybrid plasma simulation code is used to simulate the same conditions in

order to improve understanding of the experimental results.

Acknowledgements:

This work has been supported through the UK Engineering and Physical Sciences Research

Council (EPSRC) manufacturing grant EP/K018388/1 and the authors would also like to thank

Intel Ireland, Ltd. for financial support.

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simultaneous measurement of atomic oxygen densities and local mean electron energies in

radio-frequency driven plasmas, Appl. Phys. Lett. 105 234105

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Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+AS-MoA

Frontiers of Photoemission with Synchrotron and XFEL Radiation/Advances in High-resolution Imaging Techniques

Moderators: Maya Kiskinova, Elettra-Sincrotrone Trieste, Italy, Olivier Renault, CEA-University Grenoble Alps, France

1:40pm **SA+AS-MoA1 Photoemission with Soft and Hard X-Rays: Past, Present, and Future*, Charles Fadley,*** University of California, Davis **INVITED**

In this talk, I will begin by briefly reviewing some of the key early developments in soft x-ray photoelectron spectroscopy (XPS), angle-resolved XPS (ARXPS), x-ray photoelectron diffraction (XPD), and soft x-ray angle-resolved photoemission (ARPES). I will then consider combining these well-established methods with more recent techniques involving the tailoring of the x-ray wavefield through standing-wave (SW) excitation or total-reflection (TRXPS) to provide enhanced depth resolution and the use of hard x-ray excitation in the multi-keV regime (HXPS, HAXPES) to study bulk materials and buried layers and interfaces [1-5]. Applications to semiconductor- [1], oxide- [2.4,5], and magnetic- [2] heterostructures, as well as liquid/solid interfaces [3] will be considered. Future possibilities combining these approaches with variable polarization, as well as spin-, space-, and time- resolution will also be discussed.

Acknowledgements:

This work was supported by the U.S. Department of Energy, Contracts DE-AC02-05CH11231 at LBNL and DE-SC0014697 at UC Davis, and through the LDRD Program of LBNL.

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[1] "Bulk Electronic Structure of the Dilute Near-Ferromagnetic Semiconductor $Ga_{1-x}Mn_xAs$ via Hard X-Ray Angle-Resolved Photoemission" A. X. Gray, J. Minar, S. Ueda, P. R. Stone, Y. Yamashita, J. Fujii, J. Braun, L. Plucinski, C. M. Schneider, G. Panaccione, H. Ebert, O. D. Dubon, K. Kobayashi, and C. S. Fadley, Nature Materials 11, 957 (2012).

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2:20pm **SA+AS-MoA3 Honorary Session for Prof. Charles Fadley**, *O.J. Renault,* CEA-University Grenoble Alps, France*; **Julien Rault,*** Synchrotron SOLEIL, France

This contribution is intended to honor Prof. Charles Fadely for his unvaluable work in the field of photoemission over the past 50 years and will celebrate his 75th birthday. It will immediately follow his invited talk and will take the form of 3 short talks given by some of his former students.

2:40pm **SA+AS-MoA4 Ultrafast Magnetization Relaxation Dynamics in $La_{0.66}Sr_{0.33}MnO_3$ Films*, Tommaso Pincelli,*** Università di Milano, Italy*; A.Yu. Petrov, G. Panaccione,* Laboratorio TASC, IOM-CNR, Italy*; M. Oura,* RIKEN SPring-8, Japan*; T.L. Lee,* Diamond Light Source Ltd., UK*; G. Rossi,* Università di Milano, Italy

Hole-doped rare-earth manganites, like $La_{0.66}Sr_{0.33}MnO_3$ (LSMO), display exotic phenomena such as concurrent colossal magnetoresistance and half-metallicity which originate from the interplay of charge, spin, and orbital degrees of freedom [1]. The peculiar transport properties of LSMO thin films combined with the ferromagnetic order that persists up to about 350 K [2] render such system a most technologically attractive material for spin injection: the spin polarization at the Fermi level reaches about 100% for $T<T_{Curie}$ [3].

The ultrafast manipulation of spin states in LSMO can be tested by state-of-the-art time-resolved pump-probe techniques. Previous studies by optical pump-probe spectroscopy have given evidence of photoinduced effects in ferromagnetic manganites [4].

Photo-Electron Spectroscopy (PES) allows a direct measurement of the electronic structure; time-resolved PES is able to disentangle the delicate out-of-equilibrium interplay between electronic, spin and lattice degrees of freedom [5], an essential feature in the case of highly correlated materials. HArd X-ray PhotoElectron Spectroscopy (HAXPES) extends the probing depth of PES to the bulk of the solid (tens of nm), and therefore does not suffer of the modification induced by the surface.

We present here a pump-probe HAXPES study of the relaxation dynamics of LSMO thin films. We study the structure of the Mn 2p core level and, in particular, the bulk-only screening channel proportional to the metallic and ferromagnetic state in LSMO. We observe a large and 'slow' reduced lineshape change up to 200 picoseconds after the IR pumping. By comparison with all-optical techniques (Time-Resolved Magneto-Optical Kerr effect, TR-MOKE) we are able to attribute the observed quenching to a collapse of magnetic order. The sudden demagnetization reduces the mobility of electrons in the solid, inducing a localization similar to a metal-insulator transition.

Since LSMO is half-metallic, the direct exchange of energy between the optically excited electrons and the magnetic order is inhibited by the absence of final states for spin-flip scattering [3]. So we can follow the relaxation dynamics as the energy is first dissipated in the lattice and then in a reduction of the magnetic order.

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3:00pm **SA+AS-MoA5 Inelastic Background Analysis of Haxpes Spectra for Device Technology: A Non-Destructive Tool for Accessing Deeply Buried Interfaces*, Charlotte Zborowski,*** *O.J. Renault, E. Martinez, A. Torres,* CEA, LETI, MINATEC Campus, France*; Y. Yamashita,* NIMS, Japan*; G. Grenet,* Inl, Ecl, France*; S. Tougaard,* SDU, Denmark

Recently, the advent of Hard X-ray Photoelectron Spectroscopy (HAXPES) has enabled to study deeply buried interfaces [1]. It was shown that by combining HAXPES with inelastic background analysis [2], structures at a depth >50 nm can be studied. Here, we present a study on technologically relevant High Electron Mobility power Transistors Ta/Al.

The study was performed on stacks of two metal layers of aluminum and tantalum with different thicknesses deposited on an $Al_{0.25}Ga_{0.75}N/AlN/GaN$ heterostructure [Fig. 1a]. We have used the technique to non-destructively study the activation annealing. HAXPES was performed at the Spring-8 synchrotron (Japan) using 8 keV photons.

The figure shows spectra measured around Al, Ga and Ta peaks for an as deposited sample [Fig. 1b]. The calculation of inelastic background was performed using two input parameters; the IMFP, calculated using the TPP-2M formula [3] and as the spectra present marked plasmons, after the elastic peaks, we used an average of individual inelastic cross-sections, σ, which can be determined from reflection electron energy-loss spectra. The calculation of this cross-sections' average has been made according to a mixtures rule, involving the different crossed layers, which consists in a relevant way to analyze deeply buried layers. The figure shows how the modelling of the inelastic background is used to determine the in-depth distributions, which are found in good agreement with the TEM results. We have also successfully used this technique to study the effect of annealing on the diffusion of the elements at the interfaces.

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Part of this work was performed at the Nanocharacterization Platform of CEA-MINATEC (PFNC).

NIMS and Spring-8 is acknowledged for providing beamtime and the staff of the BL15-XU beamline for their assistance during the experiment. Cyril Guedj is acknowledged for providing TEM analysis and expertise.

3:20pm **SA+AS-MoA6 Soft X-ray ARPES Investigation of the Spin-polarized n-$BaTiO_3$/$SrRuO_3$ Buried interface***, **Julien Rault**, P. Le Fèvre, F. Bertran, J. Rebellato,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France

The electric field control of functional properties such as spin injection is a crucial goal in oxide-based electronics. Non-volatile switching between different electron and spin transport in a tunnel junction channel can be achieved through charge accumulation or depletion at the interfaces [1, 2]. It has been recently suggested [3] that polarization-dependent spin-injection is expected at the interface between ferromagnetic $SrRuO_3$ (SRO) and semiconducting, ferroelectric n-$BaTiO_3$ (n-BTO), paving the way for adjustable spin-injection in full-oxide devices. This fascinating effect is due to the matching of the spin-dependent Fermi surface of SRO with n-doped BTO tube-like Fermi-surface [2, 3].

To investigate this phenomenon experimentally, we use angle-resolved photoemission spectroscopy (ARPES) to access the band structure of a buried n-BTO/SRO interface. A well-known limitation of ARPES comes from its very low probing depth (< 2 nm) due to the very low electron inelastic mean free path in the usual photon range of ARPES (1-100 eV). To overcome this limitation, we use soft x-ray photons and are able to access the interface Fermi surface below a 2-nm, upward polarized BTO thin film deposited on SRO.

Using 600 eV linearly-polarized photons, we measure the band dispersion of the interface SRO through the BTO band gap along with BTO bands for higher binding energies (see Fig. 1). The SRO-related bands were not visible at lower probing depth (photon energy ca. 250 eV) showing they actually come from the interface. Clear light-polarization dependence on the energy-momentum cuts along ΓX high-symmetry direction is shown in Figure 1. This is used to assign some parts of the Brillouin zone to specific orbitals with different spin-polarization. The in-plane Fermi surface of the interface SRO for $k_z = Z$ was also acquired and showed some clear feature fitting well the calculated band structure from Liu *et al.*, see Figure 2.

These set of results is indicative of how soft x-ray ARPES is a technique of choice to probe the band structure of functional oxide interfaces. Combined with spin-resolved photoemission, which is available at our laboratory, it will help to better understand the spin polarization predicted in ferromagnetic/ferroelectric heterostructures.

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4:00pm **SA+AS-MoA8 Progress and Perspectives in Photoemission using XFEL Radiation***, **Serguei Molodtsov,*** European XFEL GmbH, Germany **INVITED**

Photoemission is today one of the most powerful techniques for investigating low-energy properties of matter from the aerosol and adsorbate nanoparticles and molecules to the surface and bulk of solid state matter with many dedicated and specialized beamlines at synchrotron radiation facilities. The upcoming ultra-brilliant FEL sources, giving access to ultrashort timescales in the fs range, in combination with the outstanding peak brilliance achieved, set the stage for novel science. Experiments on X-ray FEL sources are being pioneered and planned at low repetition rate facilities (FLASH, LCLS, SACLA, FERMI). The European XFEL that will come in early user operation already in 2017 will be characterized by laser action from 260 eV to 25 keV photon energy and above. The facility will also yield an extremely high mean brilliance with a repetition rate suitable for different modes of photoemission detection. Together with the planned for 2021 source LCLS II this will make the European XFEL unique FEL facility for photoemission studies worldwide.

In this presentation an overview of time-resolved photoemission experiments on solids that were done at XFELs so far will be given and perspectives related to high repetition rate XFEL facilities, particularly European XFEL, will be provided.

4:40pm **SA+AS-MoA10 Revealing the Origins of Non-Joulian Magnetism with High-Resolution Photoemission Microscopy***, **Alexander Gray**, R.U. Chandrasena,* Department of Physics, Temple University*; H.D. Chopra,* Department of Mechanical Engineering, Temple University **INVITED**

All magnets elongate and contract anisotropically when placed in a magnetic field, an effect referred to as Joule magnetostriction. The hallmark of Joule magnetostriction is volume conservation, which is a broader definition applicable to self-accommodation of ferromagnetic, ferroelectric or ferroelastic domains in all functional materials. Recently, a new class of single-crystalline magnets exhibiting a ‘giant’ non-volume-conserving or non-Joulian magnetostriction was discovered [1]. In this talk I will discuss the results of our recent investigations of non-Joulian Fe_3Ga alloys using high-resolution polarization-dependent photoelectron microscopy. Our results suggest that non-Joulian magnetism arises from an unusual nearly-equipartition of the crystal into nm-scale lamellar domains and domain walls within highly periodic magnetic micro-cells. We suggest that this high-energy configuration is stabilized by the strain gradients arising from CDW that offsets electronic energy by a greater amount. High-resolution x-ray magnetic circular dichroism measurements at the Fe and Ga *L* absorption edges further provide evidence of weak iron-induced magnetism on gallium atoms via negative exchange. The results are in excellent agreement with the state-of-the-art theoretical electronic-structure calculations. Our findings open up new ways for the design of alloy systems having functional magnetic properties similar to Fe_3Ga where non-Joulian magnetostriction was first reported.

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Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+2D+AS+NS+SS-MoA

Probing Topological States And Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, Chuanxu Ma, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Tuning Dirac States by Strain in Topological Insulators***, **Lian Li,*** University of Wisconsin-Milwaukee **INVITED**

Topological insulators (TIs) are distinguished by their metallic boundary states populated by massless Dirac fermions and bulk topological Z_2 index. Changes in the band topology induced by external variables such as strain, electrical field, and composition thus provide a means to tune the boundary states. As a large spin-orbit coupling is necessary to produce an inverted band gap, most TIs discovered to date are narrow gap semiconductors consisting of heavy elements. These materials typically exhibit layered crystal structure with anisotropic bonding characteristic: strong covalent bonding in-plane and weak van der Waals (vdW) bonding out-of-plane, which has been predicted to facilitate effective strain engineering of their bulk band topology.

In this talk, I will first give an overview of the opportunities and challenges in the epitaxial growth of layered TIs. Using the prototypical 3D TI Bi_2Se_3 as an example, I will show that the characteristic anisotropic bonding facilitates a spiral growth mode on virtually any substrates by molecular beam epitaxy. The coalescence of these spirals results in a high density of grain boundaries that consist of alternating edge dislocation pairs, leading to periodic in-plane stretching and compression. Using scanning tunneling spectroscopy, I will show that this local strain field strongly modifies the Dirac surface states, where in-plane compression expands the vdW gap and destroys the Dirac states.

Next, I will show our recent work on the strain engineering of Dirac edge states of epitaxial Bi bilayer films grown on three different substrates: the (111) surface of 3D TIs Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3. Using scanning tunneling microscopy/spectroscopy, I will show that for moderately strained (<6%) single Bi bilayer on Sb_2Te_3 and Bi_2Te_3, edge states are observed; while on highly compressed single Bi bilayer on Bi_2Se_3 (>8%), edge states are suppressed. These findings, supported by density functional theory calculations, demonstrate the uniform control of edge states in 2D topological insulators by strain.

2:20pm **SP+2D+AS+NS+SS-MoA3 Detection of Current Induced Spin Polarization in Topological Insulators via Four-Probe Spectroscopy***, **Saban Hus**,* Oak Ridge National Laboratory*; Y. Chen,* Purdue University*; A.-P. Li,* Oak Ridge National Laboratory

Charge currents carried by the nontrivial surface states of topological insulators (TIs) exhibit a net spin polarization due to spin-momentum locking. Electrical detection of such a spin polarization is crucial for technological applications. However, in 3D TI materials the existence of a bulk conduction channel makes it difficult to quantify the density and the spin polarization of the current carried by the surface states. Here we report in-situ, spin sensitive four-probe spectroscopy measurements on Bi_2Te_2Se single crystals. A ferromagnetic probe detects the net spin accumulation on the surface states while a set of four-probe spectroscopy measurement is used for a quantitative separation of 2D and 3D conduction. We also examine the effect of surface doping by residual gas molecules on the current induced spin polarization. Even though, the additional carriers by dopants enhance the 2D conductance in TIs they reduce the net spin polarization of current carried by topological surface states.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

2:40pm **SP+2D+AS+NS+SS-MoA4 Switching Handedness of Chiral Solitons Under Z_4 Topology**, ***Tae-Hwan Kim,*** Pohang University of Science and Technology, Republic of Korea; *S. Cheon, H.W. Yeom,* Institute for Basic Science (IBS), Republic of Korea

Chirality is a ubiquitous and interesting property of asymmetry in many fields ranging from biology, chemistry to physics. Because of its topologically distinct nature, such chiral objects in condensed matter are often topologically excited states, which are protected by system's topology and can be used to carry information robustly against external perturbations. For instance, nanoscale magnetic skyrmions, spatially localized chiral spin texture with particle-like properties in ferromagnets, have been investigated intensively as topological information carriers for next generation spintronic devices. However, logic operations using topological excitations such as skyrmions are only conceptually proposed. On the other hand, chiral solitons are recently discovered as the topologically protected edge states of one-dimensional Z_4 topological insulators [1,2], which can be exploited as topological information carriers in electronic system. In this talk, I show experimentally and directly that switching between solitons with different chirality is possible by merging them with achiral solitons [3]. I will also show that this chiral switching corresponds to the realization of topological addition of the Z_4 topological number or chirality. With their distinct topologically protected chirality, chiral solitons could uniquely be applied for robust multilevel information storage and logic operation by storing, carrying, and switching three differently topological bits of information.

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3:00pm **SP+2D+AS+NS+SS-MoA5 Spectroscopic-imaging STM Studies on Dirac-Landau Levels in the Topological Surface State**, ***Tetsuo Hanaguri,*** RIKEN Center for Emergent Matter Science, Japan **INVITED**

We show that spectroscopic-imaging scanning tunneling microscopy (SI-STM) is a powerful tool to investigate unique electronic features of massless Dirac electrons in a magnetic field.

In contrast to the conventional massive electron that is described by a single-component wave function, the massless counterpart demands the two-component wave function. In the case of the surface state of topological insulators, these two components are associated with the spin degrees of freedom, thereby governing the magnetic properties. Thus, it is highly desirable for spintronics applications to elucidate where and how the two-component nature emerges. We found that the two-component nature manifests itself in the internal structures of Landau orbits. We visualized the local density-of-states (LDOS) distributions associated with the Landau orbits in the topological surface state of Bi_2Se_3 using SI-STM. In the presence of the potential variation, Landau orbits drift along the equipotential lines, forming ring-like patterns in the LDOS images. The observed internal structures of the rings are qualitatively different from those of conventional massive electrons but are well reproduced by the calculation based on a two-component model Dirac Hamiltonian. Our model further predicts non-trivial energy-dependent spin-magnetization textures around the potential minimum. This is originated from the interplay between the two components and may provide a clue to manipulate spins in the topological surface state.

In addition to the Landau orbits, we succeeded in observing the Zeeman shift of the lowest Landau level from which precise *g* factor of the massless Dirac electron can be estimated. We performed experiments on two topological insulators, Bi_2Se_3 and Sb_2Te_2Se, and determined the surface *g* factors of them to be 18 and -6, respectively. Such remarkable material dependence suggests that the Zeeman effect is tunable by controlling the chemical composition, providing a new knob in manipulating the spins in the topological surface state.

4:00pm **SP+2D+AS+NS+SS-MoA8 The Rashba and Quantum Size Effects in Ultrathin Bi films**, ***Toru Hirahara,*** Tokyo Institue of Technology, Japan **INVITED**

Precise characterization of physical properties in nanometer-scale materials is interesting not only in terms of low-dimensional physics but also in application to devices. Due to the reduced dimensionality and symmetry, these systems possess various interesting properties that cannot be found in the bulk. In this presentation, focusing on epitaxial ultrathin bismuth films formed on a silicon substrate, we introduce an intriguing interplay of the quantum size and Rashba effects in reciprocal space. Utilizing spin- and angle-resolved photoemission spectroscopy, we observed clear Rashba-split nature of the surface-state bands in these Bi films. However, the band dispersion did not follow the simple Rashba picture and the spin-splitting was lost where they overlapped with the bulk projection. From first-principles calculations, this was explained as a change in the nature of the band-splitting into an even-odd splitting induced by the quantum size effect [1]. Furthermore, we show that the interplay of the quantum size effect and the presence of the surface state induces a complicated change in the Fermi level position of the bulk states in bismuth, which is critical in discussing the surface-state contribution in the film properties [2,3].

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4:40pm **SP+2D+AS+NS+SS-MoA10 Understanding the Microscopic Effects of Annealing in $Ba(Fe_{1-x}Co_x)_2As_2$ Superconductor**, ***Qiang Zou,*** *Z. Wu, Q. Zheng, S. Rajputł, D.S. Parker, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

By hole or electron doping of the parent iron-based $BaFe_2As_2$ compound, the high-transition temperature superconductivity emerges from the suppression of the antiferromagnetic order.[1] It was widely reported that thermal-annealing significantly improves some superconducting characteristics in $Ba(Fe_{1-x}Co_x)_2As_2$, including T_c[2] The microscopic origin of such effect is still an open question. To make a connection between the global and the microscopic behavior of the materials, we did a comparison measurement on the pair of well-characterized x, we call ' as-grown' vs 'annealed' $Ba(Fe_{1-x}Co_x)_2As_2$ crystals, and using low temperature scanning tunneling microscopy and spectroscopy (STM/S). The superconducting gap maps deducted from the dI/dV maps were compared. The gap width distribution of the as-grown sample are obviously narrower than that of the annealed one. The coherent peak position also shifted to higher value for the annealed sample. The corresponding reduced-gaps of $2\Delta/k_bT_{c1}$ are about 2.3 and 5.4 for the as-grown and annealed crystals, respectively. The difference of the reduced-gaps indicates that the pairing strength of the annealed crystal is stronger than the as-grown one.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division . A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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5:00pm **SP+2D+AS+NS+SS-MoA11 Annealing Effect on the Properties of Superconducting Parent $BaFe_2As_2$ Crystal**, ***Shivani Rajput,*** *Q. Zou, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

Understanding of electronic interactions in a parent phase of a superconducting crystal is crucial in determining the mechanism behind high Tc superconductivity. Bulk measurements show that annealing of parent $BaFe_2As_2$ crystal at 700 ^{0}C for 30 days causes a 5 K shift in magnetic transition temperature (T_N) compared to as grown crystal. To understand the effect of annealing and details of magnetic phase transition, we investigate as-grown and annealed $BaFe_2As_2$ crystals at atomic scale using a variable temperature scanning tunneling microscopy/ spectroscopy at various temperature points across T_N. Tunneling spectroscopy exhibit a ~ 0.53 eV gap type feature above T_N, while V-shape dI/dV spectra below T_N. The dI/dV mapping measurements show that as-grown $BaFe_2As_2$ crystals are electronically inhomogeneous, and averaging the differential conductance spectra over a large area does not truly represent the electronic properties of the sample at local scale, whereas annealed sample is comparatively electronically homogeneous.

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Surface Science
Room 104E - Session SS+AS+HC-MoA
Metals, Alloys, and Oxides: Reactivity and Catalysis

Moderator: David Mullins, Oak Ridge National Laboratory

1:40pm **SS+AS+HC-MoA1 Scanning Tunneling Microscopy Studies of Hydrogen adsorption on the $RuO_2(110)$ Surface*, Arjun Dahal,*** *R. Mu, Z. Dohnálek, I. Lyubinetsky,* Pacific Northwest National Laboratory

Understanding of hydrogen/oxide interactions is important for a variety of fundamental and applied processes. By using high resolution scanning tunneling microscopy (STM), we probed the adsorption of H_2 (or D_2) on model catalyst $RuO_2(110)$ surface, which has wide range of applications in heterogeneous catalysis, hydrogen storage, and many other energy related areas. Well-defined $RuO_2(110)$ surface exposes alternating rows of bridge-bonded oxygen atoms (O_b) and five-fold-coordinated Ru atoms (Ru_{cus}). STM data indicate that hydrogen molecule dissociates even at 5 K, whereas one hydrogen adatom adsorbs on top of the Ru_{cus} site (producing a hydrate, H-Ru_{cus}, species) and the second on top of the adjacent O_b site (forming a bridging hydroxyl, H-O_b, species), generating an H-Ru_{cus}/H-O_b pair. For the low hydrogen coverage, the dissociated H-Ru_{cus}/H-O_b pairs adsorb on every alternate Ru_{cus}/O_b sites adopting a (2×1) registration. When $RuO_2(110)$ surface adopts a such registration of the H-Ru_{cus}/H-O_b pairs locally, hydrogen starts to adsorb molecularly on top of the Ru_{cus} sites in between the adjacent dissociated hydrogen-pairs. With further increase of hydrogen coverage, linear arrays of H_2 molecules are formed along Ru_{cus} rows. The saturation coverage of the hydrogen on the $RuO_2(110)$ surface is observed to be ~0.75 ML, where 1 ML is designated as the Ru_{cus} site density on the stoichiometric $RuO_2(110)$ surface (5.06×10^{14} cm^{-2}). Upon annealing the hydrogen-covered $RuO_2(110)$ surface, H_2 molecules from the linear array desorb around 110 K. On the other hand, the H-R_{cus} species of H-R_{cus}/H-O_b pair transforms (via a proton transfer) into another H-O_b group, across-row from original H-O_b group, producing crosswise H-O_b/H-O_b pair at temperatures above ~250 K.

2:00pm **SS+AS+HC-MoA2 Metal Vapor Adsorption Calorimetry on Layered Ca Niobate Nanosheets: Energetics and Adsorbate Structure*, Wei Zhang,*** *J. Lownsbury,* University of Washington*; R. Uppuluri, T.E. Mallouk,* The Pennsylvania State University*; C.T. Campbell,* University of Washington

The metal/oxide interface is essential to many current and prospective technologies, including oxide-supported metal catalysts, fuel cells, photocatalysis, and nanoscale electronic contacts, so understanding the strength of metal – oxide bonding at such interfaces is of great interest. These strengths have been measured on single crystal oxide surfaces by single crystal adsorption calorimetry (SCAC) of metal atom adsorption in ultrahigh vacuum (UHV)[1] and on niobate and tantalate nanosheets by solution-based isothermal titration calorimetry during the deposition of transition metal oxide (or hydroxide) nanoparticles from their aqueous salt solutions[2,3]. These niobate nanosheets are very interesting since they are highly ordered and essentially like single crystal surfaces in that the ratio of terrace sites to defect and edge sites is huge. Furthermore, when used as supports for transition metal oxide nanoparticles, they have been shown to display unusual stability against sintering.[2,3] Here, we directly measure the adsorption energies of metal vapor on such niobate nanosheets using SCAC in UHV. Specifically, we study the adsorption of Ca and Ag vapor onto calcium niobate films that are 4 nanosheets thick (~4 nm total). Calcium atoms show a sticking probability near unity and an initial heat of adsorption of ~660 kJ/mol, much higher than the heat of bulk Ca(s) sublimation (178 kJ/mol). Low-energy ion scattering spectroscopy (LEIS), which is element-specific and probes only the topmost atomic layer, is used to investigate the resulting metal particle/film morphology. The possible chemical reactions between the metal vapor and the calcium niobate during adsorption are elucidated using X-ray photoelectron spectroscopy (XPS).

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2:20pm **SS+AS+HC-MoA3 Structure and Reactivity of Model Iron Oxide Surfaces*, Gareth Parkinson,*** TU Wien, Austria **INVITED**

Iron oxides are abundant in nature and extensively utilized in modern technologies including heterogeneous catalysis [1]. Magnetite (Fe_3O_4), for example, is the active phase of the industrial water-gas shift catalyst, while hematite (Fe_2O_3) is used as the photoanode for photoelectrochemical water splitting. In this talk I will discuss our recent investigations of the $Fe_3O_4(100)$ and $Fe_2O_3(1\text{-}102)$ surfaces using a combined experiment/theory approach. The $Fe_3O_4(100)$ surface forms a reconstruction based on an ordered array of subsurface cation vacancies that contains exclusively Fe^{3+}, and is relatively inert [2]. Although formic acid adsorbs dissociatively at regular lattice sites [3], methanol adsorption is restricted to defects containing Fe^{2+} [4]. The bulk of the talk will focus on a detailed study of water adsorption on $Fe_3O_4(100)$ by TPD, STM, XPS, UPS, DFT+U and molecular dynamics calculations. In the remaining time I will demonstrate that a bulk terminated $Fe_2O_3(1\text{-}102)$ surface can be prepared by annealing in 10^{-6} mbar O_2, and a reduced (2x1) surface forms rapidly when heating in UHV. The structure of the (2x1) reconstruction and its reactivity toward water will be discussed.

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3:00pm **SS+AS+HC-MoA5 Structure and Ethanol Reactivity of Ti-modified $CeO_x(111)$ Mixed Oxide Surfaces***, E.W. Peterson,* ***Jing Zhou,*** University of Wyoming

Ceria has been widely studied as an oxidation-reduction catalyst due to its unique redox properties and oxygen storage capacity. There has been an interest to incorporate additional metal dopants such as Ti into ceria to potentially enhance the thermal stability as well as improve the redox properties for practical applications in catalysis. This paper focuses on the fundamental mechanistic understanding of the effect of Ti dopant on the structure and reactivity of ceria using scanning tunneling microscopy, X-ray photoelectron spectroscopy, infrared spectroscopy and temperature programmed desorption techniques. In the study, submonolayer coverage of Ti was deposited on well-ordered $CeO_x(111)$ ($1.5<x<2$) thin films at room temperature. XPS studies show that Ti is oxidized to Ti^{4+} at the cost of Ce^{4+} reduction. Observation of CO IR band at 2173 cm^{-1} further confirms the presence of titania on the ceria surface. At 300 K, small atomic-like features of Ti-O-Ce linkages are present on ceria, which can coalesce into chain structures after heating to 700 K. Upon ethanol adsorption at 300 K, ethoxy was the surface intermediate observed on both oxidized and partially reduced ceria surface. With heating, it can go through the dehydration or dehydrogenation process to form acetaldehyde, ethylene, water and hydrogen products. Our studies have demonstrated that addition of Ti in ceria can affect the dehydration and dehydrogenation selectivity. Furthermore, the nature of ceria supports associated with oxygen vacancies and Ti dopants can have a promotional effect in the stability of deposited metal nanoparticles, such as Ni, and the chemical behavior toward the adsorption and reaction of ethanol. The research is sponsored

by the National Science Foundation Career Grant (Award Number: CHE1151846) and the Wyoming NASA EPSCoR (NASA Grant: NNX13AB13A).

3:20pm **SS+AS+HC-MoA6 New Insights into the Coverage-Dependent Structure and Desorption Kinetics of CO on Palladium(111)**, ***Pan Xu***, Stony Brook University; *S.-Y. Hong,* Brookhaven National Laboratory; *S. Liu,* Stony Brook University; *N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

Carbon monoxide adlayers on palladium surfaces have, since the early days of ultrahigh-vacuum surface science, served as model systems for the study of molecule–surface interactions, structure and dynamics. As part of a recent study of the dynamics of ultrafast molecule–surface energy transfer we have revisited the CO/Pd(111) system and found that it continues to teach us about the complexities of molecule–surface interactions. Specifically, it has long been known that CO adlayers assume a wide range of ordered structures on Pd(111) at low temperature (~80 K). In fact, between the (√3×√3)R30° 0.33-ML and (2×2) 0.75-ML (saturation) structures, at least 17 well-ordered structures have been identified. Until now, however, a comprehensive correlation between these structures and the thermal desorption kinetics has not been reported. In this talk we detail a systematic investigation that correlates individual temperature-programmed desorption (TPD) features with specific adlayer structural phase transitions. We report that in addition to the spectrum of previously-observed structures we have observed for the first time, to the best of our knowledge, a well-developed, ordered domain-boundary structure at a coverage just below saturation. We have assigned this structure as a c(16×2) adlayer comprised of stripes with local (2×2) structure and used density functional theory to investigate the adsorption site preferences within the adlayer. We show how our results, in combination with existing data, can be interpreted in terms of a compromise between the energy minimization that accompanies binding at high-symmetry sites and lateral repulsive interactions. Furthermore, we describe how quantifying the coverage using the integrated desorption yield areas is problematic due to difficulties in growing a fully-saturated adlayer. We attribute these difficulties to a kinetic limitation of the structural phase transitions at high coverage, and show that this limitation is easily addressed by preparing the adlayer at a somewhat elevated temperature. We also detail use of the inversion-optimization method to extract the coverage dependence of the desorption activation energy from the TPD measurements. We compare the resultant simulated TPD line shapes with those derived using the “leading-edge” analysis method.

4:00pm **SS+AS+HC-MoA8 Combined Experimental and Computational Study of Water on Fe_3O_4 (001)**, ***Jan Hulva,*** Vienna University of Technology, Austria; *M. Meier,* Universität Wien, Austria; *J. Pavelec, S. Maaß, R. Bliem, M. Schmid, U. Diebold,* Vienna University of Technology, Austria; *C. Franchini,* Universität Wien, Austria; *G.S. Parkinson,* Vienna University of Technology, Austria

The interaction of water with metal-oxide surfaces is an important topic for a wide range of technological and environmental applications. This is particularly true for the iron oxides because of their abundance in nature and their use in chemical processes where water is involved e.g. the water-gas shift reaction [1]. Recent studies of water on iron oxide surfaces have found significant complexity, with evidence for pressure dependent adsorption, mixed-mode adsorption and coverage dependent hydrogen bonding [2-4]. Here we use a multi-technique experimental approach combined with ab-initio calculations including molecular dynamics to disentangle the coverage and temperature dependent behavior of water on the reconstructed Fe3O4(001)-(√2x√2)R45° surface [5].

Temperature programmed desorption shows that the first monolayer of water desorbs from the surface in four distinct peaks between 150 K and 250 K. Based on XPS, STM images and ab-initio calculations, we conclude that the first three peaks originate from molecular water desorbing from a coverage-dependent hydrogen-bonded network, while the last peak results from recombinative desorption from a partially dissociated water trimer species. Two additional desorption states at 340 K and 520 K are ascribed to desorption from surface defects and recombinative desorption of the surface surface hydroxyl groups, respectively.

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4:20pm **SS+AS+HC-MoA9 Water Desorption from Sulfur-Doped Oxide Thin Films on W (100)**, ***Anthony Babore***, *J.C. Hemminger,* University of California Irvine

Recent first principle calculations by Pacchioni and coworkers[1] suggest that sulfur dopants incorporated into the WO_{3-} lattice could favorably shift the band gap for enhanced visible light absorption. The present study aims to gain fundamental insight into the reactivity of a simple sulfur doped tungsten oxide system by using temperature programmed desorption (TPD) and water (D_2O) as a probe molecule. Furthermore, water desorption spectra were also obtained for pure oxide and pure sulfide films on W (100) for comparison. Auger electron spectroscopy (AES) was used to confirm the presence and relative amounts of sulfur and oxygen on the surface. TPD was then used to monitor the m/z 20, 19, and 18 signal intensity as a function of the temperature. To quantify the reactivity of water on the surface, activation energies of desorption were obtained. The results indicate distinct differences in the desorption spectra and desorption energies that exemplify the reactivity of each of the surfaces.

1. Wang F, Di Valentin C, Pacchioni G (2012) J Phys Chem C 116:8901–8909

4:40pm **SS+AS+HC-MoA10 Adsorption and Decomposition of Dimethyl Methylphosphonate on Metal Oxide Surfaces Under Atmospheric Conditions**, ***Ashley Head***, *L. Trotochaud,* Lawrence Berkeley National Laboratory (LBNL); *R. Tsyshevsky,* University of Maryland College Park; *O. Karslioglu,* Lawrence Berkeley National Laboratory (LBNL); *M.M. Kuklja,* University of Maryland College Park; *H. Bluhm,* Lawrence Berkeley National Laboratory (LBNL)

Organophosphonates are used as corrosion inhibitors, pesticides, insecticides, and chemical warfare agents. This class of molecules has a range of acute toxicity, so dimethyl methylphosphonate is commonly used as a proxy for more toxic molecules. Metal oxides are used in applications for binding and decomposing organophosphonates despite little understanding of the chemistry and reactivity, especially in the presence of atmospheric molecules. With the ability to collect photoemission spectra at pressures up to about 25 Torr, ambient pressure XPS is well-suited to investigate the adsorption of DMMP in the presence of other molecules that have relevance to applications. Using MoO_x and CuO_x foils as model systems for chemical filtration materials, we have studied the adsorption and decomposition behavior of DMMP and how this behavior changes in the presence of atmospherically relevant molecules, including water, hydrocarbons, and NO_x. The effect of the small molecules on the substrate and the subsequent effects on DMMP binding, coverage, and decomposition will be discussed. APXPS results are interpreted with the aid of density functional theory calculations, which model DMMP adsorption, decomposition products, and reaction energies.

5:00pm **SS+AS+HC-MoA11 Oxygen Chemisorption and Thermal Oxidation of TiAlN High Power Pulsed Magnetron Sputtering Hard Coatings**, ***Martin Wiesing***, *T. de los Arcos, G. Grundmeier,* University of Paderborn, Germany

The thermal oxidation of $Ti_{0.5}Al_{0.5}N$ hard coatings as deposited by High Power Pulsed Magnetron Sputtering was investigated at reduced oxygen partial pressures of 10^{-6} and 10^{-2} Pa in a temperature range from 298 to 800 K. Quasi in-situ X-ray Photoelectron Spectroscopy and Low Energy Ion Scattering studies revealed oxygen to bind selectively to Ti-sites on the surface [1] and oxygen migration into the near-surface region. Three dimensional oxidation leads to the formation of a double layered surface oxide including a TiAl(O,N) growth region [2] terminated with a Ti^{IV} containing surface oxide [3]. Based on Wagner plot analysis, the surface oxide layer formed at 800 K can be described by a mixed $Ti^{IV}Al^{III}O_x$ phase while a separated $(Ti^{IV}O_2)(Al^{III}{}_2O_3)$ phase preferentially forms at 298 K. Complementary Ultraviolet Photoelectron Spectroscopy revealed a high degree of nitrogen doping in both cases.

The results are of importance for the design of multi-layered nitridic hard coatings and for a thorough understanding of the high-temperature oxidation resistance of such coatings.

Acknowledgement: The authors gratefully acknowledge the German Research Foundation (DFG) for financial support (SFB–TR 87). We thank Prof. Dr. J. Schneider and Holger Rueß for providing the coated specimen.

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Applied Surface Science
Room 101B - Session AS+AC-TuM

Practical Surface Analysis II: Microanalysis, Nanoanalysis, Atom Probe, and All Things 'Small'

Moderators: Arun Devaraj, Pacific Northwest National Laboratory, Daniel Gaspar, Pacific Northwest National Laboratory

8:00am **AS+AC-TuM1 Progress Toward Atomic-Scale Tomography*, Thomas Kelly,*** CAMECA Instruments Inc. **INVITED**

There have been efforts of late to produce three-dimensional images at the atomic scale where every atom is accounted for and the position information is quite precise. All atoms in a two-dimensional thin film of boron nitride were imaged and identified by Krivanek et al. [1]. Scott et al. were able to produce three-dimensional images using electron tomography that show every atom in a gold nanoparticle containing over 7000 gold atoms [2]. Using atom probe tomography (APT), Moody et al. have shown three-dimensional images of several million atoms in an aluminum alloy where each atom is positioned correctly in a face-centered cubic lattice and 60% of the atoms are detected [3]. These are all impressive and important developments. They suggest what atomic-scale microscopy might ultimately achieve: recording with high precision the position and identity of every atom in a technologically relevant structure. This capability can fairly be termed atomic-scale tomography (AST).

If AST is to be achieved, it appears that APT and electron microscopy should be used synergistically to capture the strengths of one technique to overcome the limitations of the other. This question has been explored in detail [4] and the conclusion is that there are some ways that AST can be achieved. The instrumental developments needed to reach AST with APT and (S)TEM as a basis include: trajectory corrections for precise atom placement and detecting 100% of the atoms without ambiguity in identity. The former may be achieved by imaging the specimen apex to enable precise ion trajectory simulation toward the detector. An electron column integrated into an atom probe can, in principle, record the specimen apex shape throughout an entire atom probe experiment. Detectors for recording all atoms might be based on superconducting materials [5]. If these detectors also record an ion's kinetic energy, then most time of flight-based ambiguities in peak identification can be eliminated [6].

Once these instruments are combined, the full analytical capabilities of each can be used synergistically. This presentation will outline approaches that should be pursued to reach this end and review the current plans to build an atomic-scale tomograph.

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9:20am **AS+AC-TuM5 Atom Probe Tomography and Electron Microscopy Investigation of Composition and Structure of Functionalized Carbon*, Chilan Ngo,*** *D.R. Diercks, M.B. Strand, S. Pylypenko,* Colorado School of Mines

Carbon is one of the most studied materials due to its broad range of properties, versatility, and low cost. Functionalization or doping of carbon with heteroatoms is an effective way to tailor the properties of carbon and further modify the material for various applications. While significant efforts have been placed on understanding the composition, structure and properties of doped carbon supports, there is a lack of understanding regarding the 3-D distribution of dopant within high surface area materials. In this work, we expand the understanding of nitrogen-functionalized carbon materials by focusing on analysis of nitrogen distribution through atom probe tomography (APT), transmission electron microscopy (TEM), and complementary characterization techniques. Specifically, APT analysis has been applied to provide unique, high-resolution insight into the composition/structure of high-surface area carbon – demonstrating feasibility of the technique towards such materials. Nitrogen-doped carbon nanospheres were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different nitrogen concentration and varied relative distribution of nitrogen functionalities. Sample preparation was performed via focused-ion beam (FIB), in order to isolate C spheres into a workable APT tip. The work presented herein provides a foundation not only for further understanding of N-doped carbon materials and N-containing nonprecious catalysts (NPMCs) employed in a variety of important catalytic reactions, but also to prepare model high-surface area materials, compatible for study via *in situ* liquid and electrochemistry TEM techniques.

9:40am **AS+AC-TuM6 Advanced XPS Imaging and Spectromicroscopy: a Review of Current Capabilities*, Olivier Renault,*** CEA-University Grenoble Alps, France

At the practical level, XPS imaging is still poorly used today. This is due to on the one hand to instrumental issues with for instance the difficulty to produce nice secondary electron images to help quick navigation at the surface; on the other hand, lower counting statistics of core-level images necessitate high transmission imaging spectrometer and in some cases post-processing of image data sets using, e.g, PCA. XPS imaging and spectromicroscopy is nevertheless complementary to ToF-SIMS and Auger as it provides quantification and chemical speciation, besides accessing the mesoscopic scale. It should therefore deserve a much broader use to better understand laterally heterogeneous systems. On some instruments, electronic band structure imaging, equivalent to ARUPS microscopy, is becoming possible in routine use, widening significantly the capabilities of photoelectron microscopy with laboratory sources for important applications, e.g., novel 2D materials. In this contribution, we will review through various examples from graphene doping [1] to oxide-based resistive memories and single layer MoS2, the current capabilities of XPS imaging and spectromicroscopy as implemented with a PEEM-based commercial instrument enabling core-level images with sub-µm scale lateral resolution. The benefits of band structure imaging for 2D semiconducting materials will be addressed [2]. Finally, perspectives regarding photoelectron microscopy with hard x-rays will be drawn [3].

This work was performed on the Nanocharacterization platform of CEA-MINATEC.

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11:00am **AS+AC-TuM10 Challenges and Solutions for Confined Volume Characterization in Semiconductor Systems*, Wilfried Vandervorst,*** IMEC & KULeuven, Belgium **INVITED**

Pushing the limits in IC-technology towards the nanometer scale, novel materials and in particular interfacial interactions in 3D-devcies play a crucial role leading to a demand for concepts suited to probe very small volumes and enable atomic scale observations.

Atom probe tomography (APT) can provide 3D-composition analysis within very small volumes (a few nm^3) with high sensitivity and accuracy. Nevertheless the presence of many materials with different evaporation fields and inhomogeneous laser-tip interactions creates tip distortions and trajectory aberrations inducing severe artefacts in reconstructed profile. Limits in mass resolving power, the presence of multiple charge states, cluster emission and variable detection efficiencies and strong laser power effects do hamper accurate and precise quantification and/or deviation from the correct composition.

Complementary to the resolving power of APT, is the application of scanning probes which enable to grasp the electrical activity of dopants or identify conduction paths within such volumes. As SPM is inherently a 2D-method, concepts for expanding into the depth dimension are explored (cfr Scalpel SPM, ion beam sputtering icw SPM) with applications in logic device engineering, failure analysis and memory cell development.

As APT and SPM suffer from a poor productivity and a lack of statistical averaging over large areas as required in more production oriented metrology. A solution can be found through ensemble measurements whereby spatial resolution is provided by the device under investigation and not by the probing beam. We will illustrate this concept through applications of "self focusing SIMS" which allows to determine the composition from trenches as small as 20 nm without having an ion beam with nm-resolution. Moreover within the area of selective area deposition SF-Sims may provide a unique analysis capability sampling defectivity of self-assembled monolayers and limited selectivity.

Similarly crystallinity in narrow trenches (< 50 nm) can be obtained through channeling RBS whereby again we use a large beam but nevertheless probe the information from an array of very fine features. In all these cases, the averaging over a large array provides excellent statistics and in some cases dramatically improved productivity through the enhanced signal versus the case of a very focused probe beam. The latter is ultimately exemplified in Raman experiments on narrow SiGe-trenches where we demonstrate that very narrow features (20 nm) provide a significantly enhanced (50-100x) compared to its blanket counterpart enabling to probe composition and structural properties from a small volume.

11:40am **AS+AC-TuM12 Characterization of Protein G B1 Immobilized Gold Nanoparticles using Time of Flight Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy**, *Y.-C. Wang,* ***David Castner,*** University of Washington

Nanoparticles (NPs) have been widely used in many fields of science due to their unique physical properties. While many applications of NPs such as imaging probes or drug carriers often require the conjugation of proteins or biomolecules, the surface interactions between NPs and biomolecules remains underexplored. For example, the immobilization of immunoglobulin G (IgG) onto nanoparticle surfaces is critical for the development of many immunosensors and drug delivery nanocarriers. Notably, the orientation of the immobilized IgG can have significant impact on the clinical outcomes of these carriers by impacting its biostability and efficacy.

In this work, Protein G B1, a protein that will selectively bind to the Fc tail of IgG, was immobilized onto gold NPs (AuNPs) functionalized with maleimide and oligo-(ethylene glycol)(OEG) self-assembled monolayers (SAMs). Protein G B1 was immobilized onto AuNPs using either carbonyldiimidazole (CDI) chemistry or through a maleimide-cysteine bond. We used the surface sensitive analysis techniques of x-ray photoelectron spectroscopy (XPS) and time of flight-secondary ion mass spectrometry (ToF-SIMS) to characterize the protein G B1 immobilization. Unlike conventional NP characterization techniques such as dynamic light scattering (DLS) and UV/Vis, XPS and ToF-SIMS can provide additional information on the surface elemental composition, protein coverage and orientation.

XPS analysis confirmed the AuNP functionalization with both the maleimide and OEG-SAMs. After incubation with protein, the immobilization of the protein was demonstrated by the increased nitrogen signal on the surface of both SAMs. Loosely bound protein on the AuNPs was effectively removed through conventional centrifugation-resuspension washes and dialysis cleaning.

ToF-SIMS analysis also confirmed the successful functionalization, CDI activation, and protein immobilization by identifying signature secondary ions from each step of the protein immobilization process. Further, by utilizing high surface sensitivity and small sampling depth (2nm) of ToF-SIMS, the orientation of immobilized protein G B1 was determined by comparing the ratio of secondary ion intensity originating from the opposite end of the protein. As expected, the non-site specific CDI chemistry did not lead to a well-defined orientation on the AuNPs. In contrast, we were able to control the orientation of the immobilized protein using maleimide functionalized AuNPs and cysteine mutants of Protein G B1. The systematic characterization of this study provided detailed information about protein-nanoparticle interactions that advances our understanding of the complex protein-NP interface.

12:00pm **AS+AC-TuM13 What's New in Wetting? Inorganic Nanotubes at a Water Interface - A Molecular View**, ***Sidney Cohen**, O. Goldbart, I. Kaplan-Ashiri,* Weizmann Institute of Science, Israel*; P. Glazyrina,* Ural Federal University, Russia*; H.D. Wagner,* Weizmann Institute of Science, Israel*; A. Enyashin,* Ub Ras, Russia*; R. Tenne,* Weizmann Institute of Science, Israel

Wetting of solid surfaces is a complex and subtle phenomenon which has been studied carefully over the past 200 years. A good understanding of wetting can explain many key physical interactions at interfaces, notable examples being in lubrication, composite materials, and capillarity. Wetting phenomena continue to intrigue the scientific community due to the complexity of this seemingly simple process. In recent years, specific nano-scale aspects of wetting have been revealed, highlighting the importance of a molecular-level understanding of wetting. The study of nanotube wetting encompasses the old/new, as well as nanoscale aspect of these endeavors. Proven importance of nanotubes as fillers in ultra-strength nanocomposites, where the interfacial interactions in the nanocomposite are controlled by wetting, lends a technological push to the field. Inorganic nanotubes (INT) formed from tungsten and molybdenum disulfides disperse very well in a variety of polymers, enabling preparation of nanocomposites with enhanced mechanical properties, thermal stability and improved rheological behavior. Nonetheless, the nature of the interaction between a nanotube and polymer liquid has received little attention and is poorly understood.Here we present a combined experimental and theoretical study on the microscopic interaction of WS_2 nanotubes (INT-WS_2) with water. The unique experimental approach is based on manipulation and pull-out of individual nanotubes from water films while monitoring the forces generated with a cantilever in an atomic force microscope (AFM). This method draws on concepts of the classic Wilhemy Balance Technique, while exploiting the exquisite force control of the AFM. The AFM experiments were contrasted with parallel experiments in an environmental scanning electron microscope (ESEM). Detailed theoretical calculations based on density functional theory (DFT) predicted well the interaction energy for large, closed cap nanotubes, but vastly underestimated the interaction energy with small, open-ended nanotubes. For those small diameter tubes, force-field molecular dynamics (MD) simulations together with a thermodynamic analysis qualitatively explain the observed behavior, strongly implicating a dominant capillary effect. Visualization of the pullout in the ESEM together with AFM force traces allow precise modelling of the meniscus formation during pullout, reflecting the energetics of the interface at, and inside the nanotube wall.**Acknowledgment:** Supported by the Israel National Nano-Initiative, the Israel Science Foundation, H. Perlman Foundation. and Act 211 Government of the Russian Federation, contract № 02.A03.21.0006.

Manufacturing Science and Technology
Room 103A - Session MS+AS-TuM

Characterization and Processing for IC Manufacturing

Moderator: Alain C. Diebold, SUNY College of Nanoscale Science and Engineering

8:00am **MS+AS-TuM1 Thermal Decomposition Properties of Bis(cyclopentadienyl)magnesium for Various Gas Supply System Materials**, ***Hidekazu Ishii,*** Tohoku University, Japan*; S. Yamashita, M. Nagase, A. Hidaka, K. Ikeda,* Fujikin Incorporated, Japan*; Y. Shiba, Y. Shirai, S. Sugawa,* Tohoku University, Japan

High purity Bis(cyclopentadienyl)magnesium(Cp_2Mg) is used as chemical vapor deposition material of semiconductor devises and dopant for obtaining p-type conduction in GaN based material devices. However, precise control of supply concentration of Cp_2Mg is very difficult because its vapor pressure is very low. Generally, Cp_2Mg is supplied from a precursor container to the film formation chamber by bubbling with the carrier gas. In this method, the tubing for the gas supply must be heated to avoid deposition of Cp_2Mg on the inner surface of tube, which leads to a concern of decomposition of Cp_2Mg. Thus, understanding of thermal decomposition properties of Cp_2Mg for various materials for gas supply tube is important. In this report, we report evaluation results of thermal decomposition properties of Cp_2Mg for various materials such as SUS316L stainless steel and Cr_2O_3, Al_2O_3-passivated stainless steel that are used for gas tubing, as well as Ni-Co alloy and Hastelloy C-22 that are used for a valve diaphragm.

8:40am **MS+AS-TuM3 High Volume Materials Characterization in the CMOS Industry**, ***Paul van der Heide,*** GLOBALFOUNDRIES **INVITED**

In no time in the past has Materials Characterization been as pivotal to CMOS device R&D as it is today. This stems primarily from the fact that since the era of *Denard scaling* (shrinkage alone), new materials/ structures have had to be introduced in order for logic devices to continue to adhere to the dimension shrinkage implied by *Moore's law* (examples lie in the introduction of strain engineering (introduced in 90nm devices rolled out in 2003), HKMG structures (introduced in 45nm devices rolled out in 2007), and 3D structures (introduced in 22nm devices rolled out in 2011)). This timeline also begs the question: A*re we not at the precipice of the next innovation?* What is certain is that the CMOS industry will experience significant and in some cases unforeseen changes over the next 2 decades.

Materials characterization is not only needed to support R&D efforts, but is also required to provide insight into manufacturing issues, along with the qualification of a) new fabrication processes, b) new process equipment, and c) process equipment coming off preventative maintenance cycles.

Paramount in these areas is analytical precision, repeatability, data quality and speed (turn around time). This stems from the other aspect of *Moore's law*; that being that the cost associated with the development/implementation of a new device node must remain financially attractive. Topics covered in this presentation include: the support requirements of a high volume CMOS manufacturing site, merits of academia versus industrial labs, financial justifications of onsite lab/s, along with some recent analytical examples/capabilities.

9:20am **MS+AS-TuM5 Dynamics in SIMS Characterization for Advanced Nano-Technology: Challenges and Solutions for Novel Materials and 3-D Devices***,* ***Marinus Hopstaken,*** IBM T.J. Watson Research Center **INVITED**

Over the last few decades, SIMS depth profiling techniques and instrumentation has tremendously evolved to keep up with developments in advanced CMOS technology. I will discuss the main technology drivers, their implications for SIMS characterization, and review some of the analytical challenges and solutions:

- Continued dimensional scaling (*i.e.* lower film thicknesses, ultra-shallow junctions USJ) demands for progressive improvement of depth resolution. This has been enabled by continuous instrumental developments to provide high-density, stable, and low-impact energy primary ions beams to enable sub-nm depth resolution (*i.e.* 'Atomic layer' SIMS). I will give various applications of high resolution SIMS analysis of thin-film stacks / USJ, routinely employing sub-500 eV ion beams

- Advanced IC development in a manufacturing context demands at-line SIMS metrology with high throughput and reproducibility, often requiring small area analysis on patterned wafers. Key enablers for advances in SIMS metrology are availability of high-density primary ion beams, high level of automation to allow for unattended operation, and instrumental stability / drift correction. I will discuss implications for high-throughput SIMS full wafer mapping and considerations for patterned device wafer

- Paradigm shift towards 3D device architectures (*i.e.* FinFET) poses one of the greatest challenges, and appears fundamentally incompatible with low-energy (*i.e.* 'broad-beam') SIMS. This can be partially circumvented by averaging over a large regular arrays of FinFET structures, in combination with backfill and planarization to delineate the Fin sidewall ('SIMS through Fin technique;), which we have successfully employed at realistic Fin dimensions and pitch, relevant for 14 nm node and beyond

- Integration of novel and dissimilar material stacks demands novel SIMS calibration methods and/or quantification protocols. Potential solutions to deal with the higher complexity are cross-calibration with absolute external techniques (ion scattering techniques, 3D-APT, advanced TEM-EDX / EELS, etc…) and multi-standard approaches for explicit correction of SIMS yield variations with matrix composition. I will give selected examples for quantification of in-situ doping in $SiGe_x$ for wide variation in Ge% and different doping species in various III-V compounds

11:20am **MS+AS-TuM11 Characterization of Electrical Properties of Si and GaN Devices using Scanning Microwave Impedance Microscopy (sMIM) and Nano-scale Capacitance-voltage Curves***,* ***Stuart Friedman****, F. Stanke, Y. Yang, O. Amster,* PrimeNano, Inc

The use of Atomic Force Microscopy (AFM) electrical measurement modes is a critical tool for the study of semiconductor devices and process development. A relatively new electrical mode, scanning microwave impedance microscopy (sMIM), measures a material's change in permittivity and conductivity at the scale of an AFM probe tip [1]. sMIM provides the real and imaginary impedance (Re(Z) and Im(Z)) of the probe sample interface. By measuring the reflected microwave signal as a sample of interest is imaged with an AFM we can in parallel capture the variations in permittivity and conductivity and, for doped semiconductors, variations in the depletion layer geometry. An existing technique for characterizing doped semicondutors, scanning capacitance microscopy, modulates the tip-sample bias and detects the tip-sample capacitance with a lock-in amplifier. A previous study compares sMIM to SCM and highlights the additional capabilities of sMIM [2].

In this talk we focus on the detailed mechanisms and capabilities of the nano-scale C-V curves that can be obtained using sMIM to measure the tip-sample capacitance as a tip-sample bias is swept. Analogous to traditional macro-scale capacitance-voltage experiments, the nano-scale C-V curves probe properties such as doping concentration through their influence on the voltage dependent geometry of the depletion layer. In particular, in this talk we will address the ability to extract semiconductor properties, such as doping concentration, from the C-V curves. This study includes analytical and finite element modeling of tip-bias dependent depletion layer geometry and impedance. These are compared to experimental results on reference samples for both doped Si and GaN doped staircases to validate the systematic response of the sMIM-C channel to the doping concentration.

[1] S. Friedman, O. Amster, Y. Yang, "Recent advances in scanning Microwave Impedance Microscopy (sMIM) for nano-scale measurements and industrial applications." Proceedings of the SPIE, Volume 9173, id. 917308 8 pp. (2014)

[2] B. Drevniok, St.J. Dixon-Warren, O. Amster, S.L. Friedman, and Y. Yang, "Extending Electrical Scanning Probe Microscopy Measurements of Semiconductor Devices Using Microwave Impedance Microscopy", Proceedings of the 41st International Symposium on Testing and Failure Analysis (2015), pp. 77.

11:40am **MS+AS-TuM12 Results of the 2016 Triennial Review of the National Nanotechnology Initiative***,* ***James Murday,*** University of Southern California*; B.R. Rogers,* Vanderbilt University*; E.B. Svedberg,* The National Academies **INVITED**

The National Nanotechnology Initiative is a multi-agency effort to advance nanoscale science, engineering, and technology and to capture the associated economic and societal benefits. The NNI comprises the collective activities and programs among the more than two dozen participating federal agencies with diverse missions and presently a total annual investment of approximately $1.5 billion. Every three years the National Academies selects a committee of experts to review the NNI in accordance with the provisions of the 21st Century Nanotechnology Research and Development Act. A report on the most recent review has just been released. This report has paid particular attention to examining and commenting on the physical and human infrastructure needs for successful realization in the United States of the benefits of nanotechnology development and also the mechanisms used by the NNI to advance focused areas of nanotechnology towards advanced development and commercialization. We will report the findings and recommendations of this review.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic

Room 103C - Session SA+2D+AC+AS+TF-TuM

Applications of Synchrotron-based Techniques to 2D Materials (8:00-10:00 am)/Complex Functional Materials and Heterostructures (11:00 am-12:20 pm)

Moderators: Nicholas Barrett, CEA Saclay, Giacomo Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **SA+2D+AC+AS+TF-TuM2 A Versatile Method for the Fabrication of 2D-electron Systems at Functional Oxide Surfaces***, T.C. Rödel,* Université Paris-Sud - SOLEIL, France*;* ***Patrick Le Fèvre,*** Synchrotron SOLEIL, France*; F. Fortuna, E. Frantzeskakis,* Université Paris-Sud - IN2P3, France*; F. Bertran,* Synchrotron SOLEIL, France*; T. Maroutian, P. Lecoeur,* Université Paris-Sud - CNRS, France*; B. Mersey,* Université de Caen, France*; A.F. Santander-Syro,* Université Paris-Sud - IN2P3, France

A critical challenge of modern materials science is to tailor novel states of matter suitable for future applications beyond semiconductor technology. In this prospect, 2D electron systems (2DESs), analogous to those created in semiconductors heterostructures, have been observed at the $LaAlO_3/SrTiO_3$ interface [1] and show amazing physical properties like metal-to-insulator transitions, superconductivity or magnetism. It was then demonstrated that 2DES could also be stabilized at the surface of $SrTiO_3$ [2] or other oxides [3], although it requires the use of intense UV or X-ray synchrotron radiation to desorb oxygen from the surface and dope it with electrons. This opened the way for the use of surface sensitive techniques, like Angle-Resolved PhotoEmission spectroscopy (ARPES) which provided a clear description of the microscopic electronic structure of the quantum well states. However, 2DESs at oxygen-deficient surfaces can be only manipulated and studied in ultra-high vacuum (to preserve the O-vacancies from re-oxidation) and thus, are not suited for experiments or applications at ambient conditions. Here we demonstrate a new, versatile and cost-effective method to generate passivated 2DESs on large areas of UHV-prepared functional oxide surfaces. It consists in a simple evaporation at room temperature of an aluminum film onto the oxide surface. Aluminum acts as a reducing agent and pumps oxygen from the substrate. It oxidizes into an insulating AlO_x layer, protecting an underlying homogeneous 2DES confined in the first atomic planes of the oxide substrate. 2 Å of Al are sufficient to create a saturated 2DES on differently oriented surfaces of $SrTiO_3$, anatase-TiO_2, or $BaTiO_3$, which were all studied by ARPES to determine the band structure (effective mass, orbital order and charge carrier densities) [4].

[1] A. Ohtomo, H. Y. Hwang, Nature **427**, 423 (2004).

[2] A. F. Santander-Syro, O. Copie, T. Kondo, F. Fortuna, S. Pailhes, R. Weht, X. G. Qiu, F. Bertran, A. Nicolaou, A. Taleb-Ibrahimi, P. Le Fèvre, G. Herranz, M. Bibes, N. Reyren, Y. Apertet, P. Lecoeur, A. Barthélémy, M. J. Rozenberg, Nature **469**, 189 (2011).

[3] T. C. Rödel, F. Fortuna, F. Bertran, M. Gabay, M. J. Rozenberg, A. F. Santander-Syro, and P. Le Fèvre, Phys. Rev. B **92**, 041106 (2015).

[4] T. C. Rödel, F. Fortuna, S. Sengupta, E. Frantzeskakis, P. Le Fèvre, F. Bertran, B. Mercey, S. Matzen, G. Agnus, T. Maroutian, P. Lecœur, and A. F. Santander-Syro, Adv. Mater. **28**, 1976 (2016).

8:40am **SA+2D+AC+AS+TF-TuM3 Advanced Spectro-microscopy of Ion Irradiated Graphene-metal Interfaces: From Substitutional Implantation to Nanobubble Formation***, **Andrea Locatelli**, A. Sala, T.-O. Menteş,* Elettra - Sincrotrone Trieste, Italy*; G. Zamborlini,* Peter Grünberg Institute (PGI-6) Jülich*; L. Patera, C. Africh,* IOM-CNR Laboratorio TASC, Italy*; M. Imam, N. Stojić, N. Binggeli,* Abdus Salam International Centre for Theoretical Physics, Italy **INVITED**

The exploitation of graphene in the next generation electronics depends on our ability of preserving and tailoring its unique electronic and transport properties. Whereas the preservation of the free-standing characteristics of graphene demands to decouple the film from its support, their modification requires functionalization and thus chemical doping. Varied methods have been devised to implant exospecies into and under the C lattice mesh. Among them, irradiation of nitrogen ions has emerged as one of the most powerful approaches, producing enhanced physical and chemical properties rather than detrimental effects. At variance with other methods, ion irradiation enables implementation of lithographic approaches for doping graphene, a feature which is most desirable for creating arrays of devices.

The characterization of complex and laterally-heterogeneous interfaces, such as that of ion-irradiated graphene, demands advanced microscopy tools. Here, we will demonstrate the present capabilities of cathode lens spectro-microscopy. As a first example, we report a proof of principle experiment demonstrating that low energy ion irradiation through an aperture can be used to achieve local control on doping in graphene. Our study tackles the fabrication of a 2-dimensional heterojunction between *n*-doped and almost neutral single-layer graphene on Ir(111). Here, XPEEM is employed to characterize the transition region between areas with metallic and semimetal-like density of states and its thermal stability [1].

Then, we will focus on the irradiation of graphene with low energy Ar and Ne ions, reporting on the formation of nanobubbles upon annealing. The morphology and local stoichiometry of the Ar-ion irradiated interface were characterized by LEEM, XPEEM and STM, specifically addressing the thermal stability of noble gas nanobubbles. These structures display a lateral size up to tens of nanometers and height of several atomic layers. Remarkably, the Ar clusters remain trapped under graphene up to temperatures nearing 1100°C, suffering no material loss through the mesh or its edges. Ab-initio calculations demonstrate that intercalated Ar undergoes extreme pressures, up to few tens GPa. The nanobubble ripening process turns out to be driven by the minimization of the energy cost of film distortion and loss of adhesion [2]. The electronic properties of the ion irradiated interface will be also discussed.

[1] A. Sala, G. Zamborlini, T.O. Menteş, A. Locatelli; Small **11**(44), 5927–5931(2016).

[2] G. Zamborlini, M. Imam , L.L. Patera , T.O. Menteş , N. Stojić , C.Africh , A. Sala , N. Binggeli , G. Comelli and A.Locatelli; Nano Lett. **15**(9), 6162–6169 (2015).

9:20am **SA+2D+AC+AS+TF-TuM5 Gas-source MBE Growth of 2D Materials Examined using X-ray Synchrotron Radiation***, **Hugh Bullen**, R.K. Nahm, S. Vishwanath, H.G. Xing, J.R. Engstrom,* Cornell University

Two-dimensional materials, in particular transition metal dichalcogenides, are attracting considerable interest from both fundamental and applied viewpoints. Here we report on the gas-source MBE growth of thin films of WSe_2 using $W(CO)_6$ and elemental Se, where we monitor the process *in situ* and in real time with X-ray synchrotron radiation. In this work, we have two independent means to introduce the thin film constituents: a (supersonic) gas-source of $W(CO)_6$ in a carrier gas of He, and an effusion cell containing elemental Se. We can collect both the scattered X-rays, and those emitted due to fluorescence. We have examined growth for a variety of conditions: growth with coincident fluxes of $W(CO)_6$ and Se, and growth in which one of the two reactant fluxes was gated. These experiments were conducted at several different substrate temperatures, on graphite (HOPG), and on so-called epitaxial graphene (graphene on SiC). First, for continuous exposure to $W(CO)_6$ and Se we observe, after an short incubation period, continuous growth of both the W and Se intensities. Analysis of this data indicates a stoichiometry consistent with WSe_2. We also find diffraction features consistent with the crystalline phase of WSe_2, where the basal plane is in the plane of the substrate. Particularly interesting is what we see when one of the reactants is gated: We have found that growth is halted by gating the incident flux of $W(CO)_6$, while the film is stable in the presence of a flux of Se_n. The physical properties of these thin films are essentially the same as those grown using continuous exposure to both reactants. We find a much different result when the flux of Se_n is gated: the absence of Se, but the presence of $W(CO)_6$, leads to *loss* of Se, and an increase in the amount of W. Since the termination of both fluxes does not lead to the loss of either element, it must be that $W(CO)_6$ is providing the species that leads to the loss of Se. The most likely scenario is that a ligand exchange reaction occurs producing the gas phase species, SeCO(*g*). Perhaps our most exciting result involves the growth of WSe_2 on epitaxial graphene. In these experiments, in addition to measuring the X-ray fluorescence, we also measured *in situ* and in real time the intensity at the anti-Bragg condition, which we have shown to be are very effective way to monitor thin film crystal growth. We observe strong and sustained oscillations, indicating layer-by-layer growth of WSe_2 of up to at least 5 monolayers. This is a very exciting result, and it indicates the effective use of synchrotron radiation to examine the growth of TMD thin films.

9:40am **SA+2D+AC+AS+TF-TuM6 Nanostructured Surface of Multilayer Graphene on Cubic-SiC***, **Victor Aristov**,* ISSP RAS, Chernogolovka, Russia, Russian Federation*; H.-C. Wu,* BIT, Beijing, China*; O.V. Molodtsova, S.V. Babenkov,* DESY, Hamburg, Germany*; A.N. Chaika,* ISSP RAS, Chernogolovka, Russia, Russian Federation

The results of atomically resolved scanning tunneling microscopy, low energy electron diffraction, low energy electron microscopy, micro-LEED and angle resolved photoelectron spectroscopy studies of graphene synthesized on cubic-SiC will be presented. Uniform few layer graphene was fabricated on SiC/Si wafers using Si-atom sublimation followed by SiC surface layer graphitization during high-temperature annealing in ultrahigh vacuum. Using the new dynamic-XPS end-station, based on the Argus spectrometer installed on the high-brilliance soft X-ray P04 beamline at PETRA III (DESY) one can control layer-by-layer graphene growth in real time following the evolution of the photoemission spectra with an acquisition time of ~ 0.1 sec/spectrum. Recording spectra during graphene growth on the SiC/Si(001) wafer, one can stop the process as soon as the desired number of graphene layers is reached. Angle-resolved photoemission measurements allowed us to extract the information about the electronic structure and the stacking order of the few-layer graphene on SiC(001). The preferential directions of the nanodomain boundaries coincide with the directions of carbon atomic chains on the SiC(001)-c(2x2) reconstruction, fabricated prior to graphene synthesis. Electrical measurements conducted on the vicinal SiC(001) samples demonstrate the opening of a transport gap in the nanostructured trilayer graphene. Our measurements demonstrate that the self-aligned periodic NBs can induce a charge transport gap up to 1.3 eV at low temperatures. The transport gap opening produces high current on-off ratio of 10^4. This development may lead to new tuneable electronic nanostructures made from graphene on cubic-SiC, opening up opportunities for a wide range of new applications.

This work was supported by the RAS, RFBR grants No 140200949 and 140201234, by the BMBF-Project No. 05K12GU2, PSP-Element No. U4606BMB1211, by a Marie Curie IIF grant No 12/IA/1264, by SPP 1459 of DFG.

11:00am **SA+2D+AC+AS+TF-TuM10 Full-field Photoelectron Spectromicroscopy of Ferroelectric Surfaces***, **Nicholas Barrett**,* CEA Saclay, France **INVITED**

Advanced low energy electron optics combined with synchrotron radiation has transformed photoelectron emission microscopy (PEEM) into a powerful technique for the microscopic study of material surfaces. High lateral, wave-vector and energy resolution makes it possible to probe spatial variations in the chemical and electronic structure of nanoscale materials.

Perovskite based ferroelectrics are one important family of oxide materials requiring such analysis. Their robust polarization, switchable by an external field, makes them extremely interesting candidates for post-CMOS electronics.

First, the principles of fully energy filtered PEEM will be presented. By a combination of both direct and reciprocal space imaging the surface charge, work function, topography, chemistry and band structure of ferroelectric materials can be studied. This will then be illustrated by several examples.

The surface charge and hence the ferroelectric polarization can be estimated from the the work function as measured in PEEM. There is a critical film thickness in BiFeO$_3$ below which the film polarization drops to zero despite constant tetragonality, suggesting the formation of stripe domains in ultra-thin films [1].

The band structure of ferroelectric domains in BaTiO$_3$(001) are studied using spatially resolved reciprocal space PEEM and synchrotron radiation. The dispersion relations can be correlated with domain chemistry and in- and out-of-plane ferrolectric polarization [2].

The ferroelectric stability as a function of temperature of piezo force microscopy written domains has been studied using threshold PEEM. A Curie temperature of 490°C is recorded which is also dependent on the poling voltage.

We will conclude with a brief demonstration of an operando PEEM experiment, opening up the perspective of studying the changes in functional oxide properties under electric stimulation.

[1] J. Rault, W. Ren, S. Prosandeev, S. Lisenkov, D. Sando, S. Fusil, M. Bibes, A. Barthélémy, L. Bellaiche and N. Barrett, Physical Review Letters 109, 267601 (2012)

[2] J. E. Rault, J. Dionot, C. Mathieu, V. Feyer, C. M. Schneider, G. Geneste, and N. Barrett, Physical Review Letters 111, 127602 (2013)

11:40am **SA+2D+AC+AS+TF-TuM12 Electron Confinement at Magnetic Oxide Interfaces: Insight from Photoemission Spectroscopy***, **Martina Mueller**,* Forschungszentrum Juelich GmbH, Germany **INVITED**

Recent advances in the fabrication of oxide heterostructures with atomic-scale precision has enabled interface and size control of complex oxide materials, for which unique phenomena with no bulk analogues have been demonstrated. In designated heterostructures, two-dimensional electron systems can be confined at oxide interfaces -- typically along the growth direction – which offer possible alternatives to conventional semiconductors in terms of functional (e.g. spin-polarized) electronic transport properties. Using redox-controlled synthesis [1, 2], the electronic properties of oxide heterostructures and interfaces can be engineered -- in terms of quality that were thought to be unique to semiconductors.

The basic idea of electron confinement applies to complex oxides just as to conventional semiconductors, but the physics is much richer. In metal oxides, confined electrons are subject to strong electron-electron interactions leading to a variety of physical phenomena that can be accessed, modified and controlled. For example, using oxides with intrinsic magnetic order allows to explore spin-related phenomena in low dimensions.

We present how to create two-dimensional electronic systems (2DES) in all-oxide heterostructures using EuO, a ferromagnetic insulator [1]. By interfacing Eu metal to SrTiO$_3$, a non-magnetic insulator, a redox reaction takes place at the interface which involves the oxidation of Eu metal into ultrathin EuO [2], and the reduction of Ti cations. This redox process strongly suggests that mobile electrons are created at the resulting interface. Using synchrotron-based soft, hard and angle-resolved photoemission spectroscopy [3] we probe the electronic structure and chemical composition at the EuO/STO interface and give a direct indication of a redox-created 2DES. The observed electronic confinement in all-oxide heterostrctures provides a route for controlling spin functionality for emerging applications.

[1] G. Prinz, T. Gerber, A. Lorke, M. Müller, submitted (2016)

[2] T. Gerber, M. Müller *et al*, J. Mater. Chem. C, 4, 1813 (2016)

[3] M. Müller *et al*, J. Electron Spectrosc. Relat. Phenom. 208, 24 (2016)

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale

Moderator: Tae-Hwan Kim, Pohang University of Science and Technology

8:00am **SP+AS+MI+NS+SS-TuM1 *In Situ* Probing of Oxygen Vacancy Diffusion Across Multilayer Oxide Heterostructures***, J. Zhu,* University of Massachusetts - Amherst*; J.-W. Lee, H. Lee,* University of Wisconsin - Madison*; R. DeSouza,* RWTH Aachen University, Germany*; C.-B. Eom,* University of Wisconsin - Madison*; **Stephen Nonnenmann**,* University of Massachusetts - Amherst

Complex oxide heterostructures display an extraordinary array of exotic collective and correlated physical phenomena that result from exploiting the strong interplay between structural and electronic degrees of freedom. Oxygen vacancies often facilitate or govern the interfacial phenomenon observed at or across well-defined discrete interfaces, ranging from domain wall pinning within ferroic systems to electron donors in conducting systems. Realization of multifunctionality within oxide heterostructures therefore necessitates a direct, proper understanding of the interrelationship exhibited by concomitant, defect-mediated transport mechanisms with adequate spatial resolution. Here we utilize a modified, *in situ* scanning probe technique to measure the surface potential across a multi-layered yttria-stabilized zirconia / strontium titanate (YSZ/STO) heterostructured film at 500 °C. Subsequent application of a classic semiconductor dopant formalism to the work function profile derived from the surface potential enables mapping of the oxygen vacancy distribution within STO with a resolution < 100 nm. The results presented herein demonstrate the promise of *in situ* scanning surface potential microscopy (SSPM) to investigate complex oxide interfacial systems multilayers that exhibit vacancy-dominated properties, under extreme environmental perturbation, on a highly localized scale.

8:20am **SP+AS+MI+NS+SS-TuM2 Study of Surface Chemistry on Various Noble Metal Surfaces by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy***, **Naihao Chiang**,* Northwestern University*; D. Chulhai,* Pennsylvania State University*; G. Goubert, L. Madison, X. Chen, E. Pozzi, M.C. Hersam, T. Seideman,* Northwestern University*; N. Jiang,* University of Illinois at Chicago*; L. Jensen,* Pennsylvania State University*; G. Schatz, R.P. Van Duyne,* Northwestern University

During the last few years, there has been an explosion of interest and activity in the field of nanoscale vibrational spectroscopy. Tip-enhanced Raman spectroscopy (TERS) combines the ability of scanning tunneling microscopy (STM) to resolve atomic scale surface features with the single molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS). The goal is to understand and manipulate chemistry on the nanometer length scale using the properties of the collective electronic excitations in noble metal nanostructures, known as localized surface plasmon resonance (LSPR).

Two recent advances in ultrahigh vacuum (UHV) TERS which illustrate the power of this nanoscale vibrational spectroscopy will be presented. First, our current understanding of the adsorbate-surface and adsorbate-plasmon interactions involved in the UHV-TERS of the N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI) on various single crystal surfaces (Ag(111), Ag(100), Cu(111), and Au(111)) which probed by a Ag tip will be discussed. This study demonstrates that TERS is a substrate general technique. Additionally, the LSPR of the Ag tip-Ag sample junction is as broad as a Ag nanoparticle dimer system. Therefore, TERS on Ag tip-Ag sample systems is also excitation general.

Second, new insights into the nature of a conformational dynamics involved at room temperature will be described. We have interrogated the conformational change of *meso*-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H$_2$TBPP) on a Cu(111) surface between two stable conformations. At room temperature, the barrier between the porphyrin ring buckling up/down conformations of the H$_2$TBPP-Cu(111) system is easily overcome, and our group has achieved unprecedented sub-nm resolution by simultaneous UHV-TERS and STM analysis. This topic illuminates that TERS can unambiguously distinguish the conformational differences between neighboring molecules with single molecule resolution. Furthermore, the sub-nm resolution led to the direct observation of single molecule transitions between states from one scan to the next.

8:40am **SP+AS+MI+NS+SS-TuM3 Exploring Surface-assisted Reactions Toward Functional Carbon Nanostructures***, Xiaohui Qiu,* National Center for Nanoscience and Technology, China **INVITED**

Understanding the dehydrogenation and dehalogenation reactions of molecular entities on surface is essential for the controlled synthesis of carbon-based nanostructures. Delicately designed precursor molecules exploit the potential of selective activation of functional groups and templating effect of substrates and promise the fabrication of nanoscale building blocks with desired geometries. Here we employed a combination of scanning tunneling microscopy, atomic force microscopy, and theoretical calculation to elucidate self-assembling of halogen-containing molecules on metal surfaces. Metallo-supramolecular assemblies are constructed via coordination bonding between metal atoms and halogen ligands. The spontaneously formed molecular scaffolds are further explored to program the structure and chemical composition of hybrid carbon architecture. We reveal the hierarchic reaction pathway of a few aromatic derivatives in an effort toward realizing carbon-based nanostructures with controllable electronic, optical and magnetic properties.

9:20am **SP+AS+MI+NS+SS-TuM5 Landscapes in Conversion of Quasi-Free-Standing Polymer Chains to Graphene Nanoribbons***, Chuanxu Ma,* Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; L. Liang,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; K. Hong, B.G. Sumpter, A.-P. Li,* Oak Ridge National Laboratory

Although the cyclodehydrogenation is well known as a key step in the bottom-up preparation of graphene nanoribbons (GNRs), the mechanism is still unclear. To understand and control the cyclodehydrogenation can help to create novel intraribbon heterojunctions of GNR-based structures. Here, we demonstrate the conversion of quasi-free-standing polymer chains to GNRs induced by thermal annealing and manipulations with a scanning tunneling microscope tip. Combined with the density functional theory calculations, a domino-like fashion and the hole-involved cyclodehydrogenation are proposed for the thermal annealing and tip-induced conversion of polymer chains to GNRs, respectively. Our results provide the first direct experimental evidence that the catalytic effect of the Au substrate is critical to the thermal-induced cyclodehydrogenation in forming bottom-up GNRs. Strongly localized density of states in the short GNR segment of the polymer–GNR herterojunction is observed. The significant confinement of the charge carriers is attributed to the big bandgap difference between the two segments of the heterojunction. Our findings might pave new ways to form GNR-based intraribbon heterojunctions by controlling the cyclodehydrogenation during bottom-up preparation, and shed light to the potential applications of the polymer–GNR herterojunctions.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and partially supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US DOE.

11:00am **SP+AS+MI+NS+SS-TuM10 Imaging Single Molecule Chemistry***,* ***Wilson Ho****,* University of California Irvine **INVITED**

Single molecule chemistry can now be probed at unprecedented spatial resolution with a low temperature scanning tunneling microscope (STM) in ultrahigh vacuum. Advances in this field have provided new measurements and insights into the structure and function of molecules through real space imaging and high resolution vibrational spectroscopy. The combination of the STM with optical spectroscopy and femtosecond lasers has added a new dimension of time to space and enabled the probing of single molecule dynamics in light-matter interaction with better than 0.1 nm resolution. The ability to visualize single molecule chemistry has reinvigorated the study of molecules and their transformations on solid surfaces. Much of the scientific advancement and understanding in surface chemistry have derived from the well-defined conditions that have long been championed by surface science in providing unambiguous results that are appealing to the theoretical and experimental communities. Imaging single molecule chemistry has a broader impact on general chemistry due principally to direct visualization of molecules and their inner machinery at the limit of space and time.

11:40am **SP+AS+MI+NS+SS-TuM12 Atomic Force Microscopy: A Tool for Chemical Analysis of Surfaces and Molecules on Atomic Scale***, Pavel Jelinek,* Institute of Physics of the AS CR, Czech Republic **INVITED**

Atomic resolution and manipulation is routinely achieved by both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) nowadays. Despite of large activities in development of the scanning probe technique, still some challenges remain, namely the chemical analysis on atomic and molecular level.

First, we will present a novel method extending further the chemical analysis [1,2] by means of AFM. Namely we will discuss a new methodology to measure Pauling's electronegativity of individual atoms on surfaces using AFM. Electronegativity has been an important concept in chemistry, originally defined by Pauling as "*the power of an atom in a molecule to attract electrons to itself*". However, its experimental determination on individual surface atoms was not possible so far.

Second, we will discuss the origin of sub molecular AFM/STM resolution acquired with functionalized tips. We will show that the electrostatic force can substantially affect the sub molecular contrast. We will show, that the electrostatic potential on a single molecule can be mapped out with sub molecular resolution.

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[5] P. Hapala et al. Nature comm. (accepted 2016)

Surface Science
Room 104D - Session SS1+AS+HC+NS-TuM

Surface Dynamics, Non-Adiabaticity, and Theory and Modeling of Surface and Interfacial Phenomena

Moderator: Greg Kimmel, Pacific Northwest National Laboratory

8:00am **SS1+AS+HC+NS-TuM1 Graphene-Semiconductor Catalytic Nanodiodes for Quantitative Detection of Hot Electrons Induced by a Chemical Reaction***, Hyosun Lee*[*]*,* KAIST & IBS, Republic of Korea*; I. Nedrygailov,* IBS & KAIST, Republic of Korea*; Y.K. Lee, C. Lee,* KAIST & IBS, Republic of Korea*; H. Choi,* Electronics and Telecommunications Research Institute (ETRI), Republic of Korea*; J.Y. Park,* Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Direct detection of hot electrons produced by exothermic reactions on catalysts is an effective strategy to quantify the non-adiabatic energy transfer during the elementary steps of the surface reactions, which provides an insight of the catalytic activity.[1,2] In particular, hot electron dynamics at the surface of metal nanoparticles (NPs) with precisely controlled shape and size is a challenge as well as a key issue in the real-world catalyst system. Herein, we show a novel scheme of graphene catalytic nanodiode composed of a Pt NPs array on graphene/TiO_2 Schottky nanodiode, which allows detection of hot electron flows induced by hydrogen oxidation on Pt NPs. By analyzing the correlation between the turnover rate (catalytic activity) and hot electron current (chemicurrent) measured on the graphene catalytic nanodiodes, we demonstrate that the catalytic nanodiodes utilizing a single graphene layer for electrical connection of Pt NPs are beneficial for the detection of hot electrons due to not only atomically thin nature of graphene but also reducing the height of the potential barrier existing at the Pt NPs/graphene interface. Thereby, the graphene catalytic nanodiodes offer an effective and easy to use approach to study mechanisms of chemical energy conversion in various heterogeneous system, even including composite catalysts with carbon-based supports.

References

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8:20am **SS1+AS+HC+NS-TuM2 Adlayer-Structure Dependent Ultrafast Desorption Dynamics: The Coverage Dependence of Substrate–Adsorbate Energy Transfer in Carbon Monoxide on Pd(111)***, Sung-Young Hong,* Brookhaven National Laboratory*; P. Xu,* Stony Brook University*; N.R. Camillone, M.G. White, N. Camillone,* Brookhaven National Laboratory

We have conducted a detailed investigation of the coverage dependence of the ultrafast photoinduced desorption of CO from the (111) surface of

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[*] **National Student Award Finalist**

palladium. Because the CO binding site depends on coverage, these measurements present an opportunity to examine the dependence of the substrate–adsorbate energy transfer on adsorption site. Specifically, as the CO coverage is increased, the adsorption site population shifts from all three-fold hollow (up to 0.33 ML), to bridge and near bridge (> 0.5–0.6 ML) and finally to mixed three-fold hollow plus top site (0.6 ML to saturation at 0.75 ML). We show that between 0.24 and 0.75 ML this progression of binding site motifs is accompanied by two remarkable features in the ultrafast photoinduced desorption of the adsorbates: (i) a roughly two-orders of magnitude increase in the desorption probability, and (ii) a nonmonotonic variation in the adsorbate–substrate energy transfer rate observed in two-pulse correlation experiments, with a minimum occurring at intermediate coverages. Simulations using a phenomenological model to describe the adsorbate–substrate energy transfer in terms of frictional coupling indicate that these features are consistent with an adsorption-site dependent electron-mediated energy coupling strength, η_{el}, that decreases with binding site in the order: three-fold hollow > bridge and near bridge > top site. The weakening of η_{el} largely counterbalances the decrease in the desorption activation energy that accompanies this progression of adsorption site motifs and moderates what would otherwise be a rise of several orders of magnitude in the desorption probability. Furthermore, we show that within this framework, the observed energy transfer rate enhancement at saturation coverage is due to interadsorbate energy transfer from the copopulation of molecules bound in three-fold hollows to their top-site neighbors. This conclusion is supported by comparison to desorption of CO from mixed CO+O adlayers where the O adsorbs at three-fold hollow sites and further promotes CO desorption from top sites.

8:40am **SS1+AS+HC+NS-TuM3 Evidence for a Spin Accelerated Reaction Mechanism in the Thermal Decomposition of Alkyl Radicals on the Si(100) Surface**, *A.J. Pohlman, D.S. Kaliakin, S.A. Varganov,* ***Sean Casey,*** University of Nevada

Density functional theory and complete active space self-consistent field calculations were used to probe the thermal decomposition of alkyl radicals on the Si(100) surface. Single dimer and single row double dimer cluster models were used to mimic the Si(100) surface in the calculations, and results indicate an interdimer β-hydrogen elimination reaction is the kinetically favored thermal decomposition pathway for adsorbed alkyl radicals. This pathway occurs via a spin crossing from the initial singlet energy surface to the triplet surface mediated by spin-orbit coupling. On the triplet surface the barrier to the elimination reaction is predicted to be about 40 kJ/mol lower than on the singlet surface. Experimental thermal desorption studies of alkyl chlorides adsorbed onto the Si(100)-(2x1) surface appear to give desorption energies for alkene products that are consistent with the barriers computed for the interdimer β-hydrogen elimination spin accelerated reaction mechanism. Experimental and computational results for the adsorption/desorption energetics of several different alkyl radicals will be discussed, along with results from partial deuteration studies of adsorption of selected haloalkanes.

9:00am **SS1+AS+HC+NS-TuM4 Hyperthermal Ion Induced Hot Carrier Excitations in a Metal Probed using Schottky Diodes**, ***Dhruva Kulkarni,*** *D.A. Field, D.B. Cutshall, J.E. Harriss, W.R. Harrell, C.E. Sosolik,* Clemson University

We present measurements on hot carrier excitations in a metal irradiated by hyperthermal energy ions.

Specifically, alkali (Na^+/Rb^+) and noble gas(Ar^{q+}) ions were used to irradiate a Schottky diode consisting of

a thin film of Ag (~25nm) grown on an n-type Si (111) wafer. Measurements of the resultant current

through the device were performed as a function of energy, angle of incidence and velocity of the

incident ions. Energy loss of the incident energetic ions inside the metal film leads to the generation of

hot carriers that travel ballistically to the Schottky interface and are detected as a kinetically-induced

current or "kinecurrent" within the device. This kinecurrent is analogous to previous measurements of

"chemicurrent" [H. Nienhaus, *Surface Science*, **45**, 1-78 (2002)], which were linked to the energy

delivered to a surface by exothermic reactions that could non-adiabatically couple to the electronic

structure and generate hot carriers.

9:20am **SS1+AS+HC+NS-TuM5 H Atom Scattering, Adsorption, and Absorption in Collisions with Metal Surfaces: the crucial role of electron-hole-pair excitation**, *M. Alducin,* Donostia International Physics Center, Spain; ***Daniel Auerbach,*** Max Planck Institute for Biophysical Chemistry, Germany; *M. Blanco-Rey,* Donostia International Physics Center, Spain; *O. Bünermann, Y. Dorenkamp,* Georg-August University of Göttingen; *S.M. Janke,* Max Planck Institute for Biophysical Chemistry, Germany; *H. Jiang,* Georg-August University of Göttingen; *A. Kandratsenka,* Max Planck Institute for Biophysical Chemistry; *G-J. Kroes,* Leiden Institute of Chemistry, The Netherlands; *M. Kammler,* Max Planck Institute for Biophysical Chemistry; *M. Pavenelo,* Leiden Institute of Chemistry **INVITED**

When an H atom collides with a solid surface, it can transfer some of its kinetic energy into elementary excitations of the solid like phonons and electron-hole pairs. If the atom loses enough kinetic energy, it can become bound to the solid, either on the surface or in the bulk. For a metal, the availability of a continuum of low lying electronic excitations can lead to the breakdown of the adiabatic Born Oppenheimer approximation and the facile nonadiabatic excitation of electron-hole pairs (ehp). If the H atom loses sufficient energy, it can enter a bound state with the solid, either on the surface or in the bulk.

We have used a combined theoretical and experimental approach to elucidate the relative roles of adiabatic processes (phonon excitation) and nonadiabatic processes (ehp excitation) in collisions of H atoms with metals, insulators, and graphene. The experiments use photolysis to produce nearly mono-energetic beams of H atoms with energies of 1 - 3.3 eV and high resolution energy loss measurements using Rydberg atom tagging time-of-flight analysis. The theory involves calculations of classical trajectories for H atom collisions with two techniques. In the first, we calculate energies and forces on-the-fly during the course of a trajectory using density functional theory (DFT) and ab initio molecular dynamics (AIMD). In the second, we construct a full dimensional potential energy surface (PES) using a flexible functional form fit to DFT energies and bulk properties of the solid.

The measured mean energy loss for H atoms scattering from metals is large, approximately 30% of the initial energy and there is a tail in the energy loss distribution (ELD) extending to the full energy of incidence. The measured ELD is in reasonable agreement with theory only if nonadiabatic effects are included; adiabatic theory drastically underestimates the energy loss. Scattering from insulators (where ehp excitation can be excluded) shows much smaller energy loss and results consistent with adiabatic theory.

For metals, nonadiabatic effects not only dominate the energy loss process, but also change both the magnitude and mechanism for adsorption on metals. With nonadiabatic effects, the most probable pathway to adsorption is for H atoms to penetrate the surface, lose energy in the subsurface region, and then reemerge to adsorb on the surface.

11:00am **SS1+AS+HC+NS-TuM10 Progress in Characterizing Submonolayer Island Growth: Capture-Zone Distributions, Growth Exponents, and Transient Mobility**, ***Theodore L. Einstein,*** University of Maryland, College Park; *A. Pimpinelli,* Rice University; *J.R. Morales-Cifuentes,* Unversity of Maryland, College Park; *D.L. González,* Universidad del Valle, Colombia

Analyzing capture-zone distributions (CZD) using the generalized Wigner distribution (GWD) has proved a powerful way to gain insight into epitaxial growth, in particular to access the critical nucleus size *i*, as reviewed in [1]. The CZ of an island contains all points closer to that island than to any other and is known as a Voronoi tesselation. This approach complements measurements of the growth exponent α from the scaling (with flux *F*) of island density $N \sim F^{\alpha}$ and of the distribution of island sizes. We summarize some extensive Monte Carlo simulations and experiments, especially newer ones, on various systems to which the GWD has been applied. These experiments include atomic or organic adsorbates, sometimes with impurities, and colloidal nano-particles. In some cases, most notably parahexaphenyl (6P) on sputter-modified mica [2], the value *i* extracted from CZD) differs from the [larger] values of *i* deduced from $N \sim F^{\alpha}$. Furthermore, while the scaling was good, the values of α differed considerably at small and large *F*, which was attributed to DLA and ALA dynamics [2]. To reconcile the CZD and scaling measurements, we took into account long-known transient mobility (hot precursors) using a rate-equation approach [3]. We also applied this method to data for pentacene (5A) on the same substrate. In applications of the GWD to social phenomena, notably the areas of secondary administrative units (e.g. counties or French *arrondissements*) [4], lognormal distributions (typically due to multiplicative noise) sometimes arise instead of GWD or gamma distributions; we show this also occurs for some pore-size distributions [5].

*Work at UMD supported by NSF CHE 13-05892

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11:20am **SS1+AS+HC+NS-TuM11 Hindered Translator and Hindered Rotor Models for Calculating the Entropy of Adsorbed Species**, ***Lynza H. Sprowl***[*], Oregon State University; *C.T. Campbell,* University of Washington; *L. Arnadottir,* Oregon State University

Adsorbed species on surfaces are important for a range of applications including heterogeneous catalysis, corrosion processes, and film growth. The need for a fast and accurate way to predict equilibrium constants and rate constants for surface reactions is important for understanding reaction kinetics and for building microkinetic models of catalytic reactions. Here a method to calculate partition functions and entropy of adsorbed species is presented. Instead of using the vibrational frequencies estimated from density functional theory and the harmonic oscillator approximation to calculate the partition function for all modes of motion, we use hindered translator and hindered rotor models for the three modes of motion parallel to the surface, two translations and one rotation. The energy barriers for translation and rotation were determined using density functional theory and the nudged elastic band method for four different adsorbates on a platinum surface: methanol, propane, ethane, and methane. The hindered translator model was used to calculate the entropy contributions from the two translations parallel to the surface and the hindered rotor model was used to calculate the entropy contribution from the rotation about the axis perpendicular to the surface. When combined with the vibrational entropy contributions and the concentration related entropy contributions, this gives the total entropy of the adsorbate on the surface. The total adsorbate entropies were found to agree well with experimental results, with an average absolute value of the error of only 1.1R or 8% for the four adsorbates. This new model should be useful to future researchers in surface chemistry, since it provides more accurate predictions of standard-state entropies and partition functions, and thus more accurate equilibrium constants and rate constants for surface reactions than provided by the standard harmonic oscillator approximation.

11:40am **SS1+AS+HC+NS-TuM12 Stabilization of *X*-Au-*X* Complexes on the Au(111) Surface: A Theoretical Investigation and Comparison of *X*=Sulfur, Chlorine, Methythiolate, and Silylthiolate**, *J. Lee, J.S. Boschen, T.L. Windus, P.A. Thiel, J.W. Evans,* ***Da-Jiang Liu,*** Iowa State University

The involvement of Au atoms in the self-assembled methylthiolate (CH_3S) monolayers on Au(111) has been demonstrated experimentally [1], while for S and Cl, chain-like structures with no direct Au involvement were found [2,3]. We find that for S on various coinage metal surfaces, the linear S-M-S complexes (M=Cu, Ag, Au) are prevalent. A systematical theoretical study of the X-Au-X complexes, with X=S, Cl, CH_3S, and SiH_3S, has been performed using DFT and other quantum chemistry methods. Assuming equilibration of the metal substrate, the chemical potential of X are calculated and used to predict the stability of various Au-X complexes. We find good agreement between DFT and available experimental findings. Furthermore, the van del Waals interaction is shown to play a crucial role in the self-assembly of CH_3S observed in experiments [1].

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12:00pm **SS1+AS+HC+NS-TuM13 Contrasting Phonon Confinement and Interface Stability at Fe-Ag and Fe-Cr Multilayers: Insights from *Ab Initio* Calculations**, *S. Hong,* ***Talat Rahman,*** University of Central Florida

We have performed density functional theory based calculations to compare the characteristics of the interface of Fe-Ag and Fe-Cr multilayers. A perfect interface lattice match between the Fe and Ag layers was obtained by rotating fcc Ag(100) layers by 45° on bcc Fe(100). On the other hand, the Fe-Cr interface could be modeled by epitaxial layers of bcc Fe(100) and Cr(100). In Fe-Ag multilayers, we find the signature peak of Fe bulk phonons (35 meV) to be completely diminished, while the low energy peaks are remarkably enhanced, in agreement with experiment [1]. In contrast, the phonon density of state in the Fe-Cr multilayers do not show any salient feature except a slight decrease in the 35 meV peak for the Fe layer at the interface, as compared to that of the middle Fe layer, again in agreement with experiment [2]. The magnetic moment of the interfacial Fe atoms is larger than that of Fe atoms in other layers, as a result of charge transfer from Fe to Ag at the interface. As compared to the middle layers, more spin-up and less spin-down states are occupied at the interface in such a way that Fe donates a large number of spin-down electrons to Ag but receives only a few spin-up electrons from the latter because of the almost fully occupied Ag d-band. This leads to rather unstable Fe-Ag interface. On the contrary, at the Fe-Cr interface, Cr can easily give and take electrons leading to smooth interfacial coupling and stable environment.

[1] B. Roldan Cuenya et al., to be published

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Surface Science
Room 104E - Session SS2+AS+HC+NS-TuM

Nanostructures: Growth, Reactivity, and Catalysis

Moderator: Bruce Koel, Princeton University

8:00am **SS2+AS+HC+NS-TuM1 Use of Size Correlations to Probe Reaction Mechanisms on Size-selected Model Catalysts**, ***Scott Anderson,*** University of Utah **INVITED**

The ability to prepare model catalysts by deposition of mass-selected metal clusters allows the size and density of catalytic sites to be varied independently and precisely, providing a new tool for mechanistic studies. In addition, preparation of truly monodisperse samples alters the kinetics for Ostwald ripening, thus changing the cluster stability under thermal/reactive conditions. This talk will focus on use of size-dependent correlations between catalytic activity and physical properties such as cluster morphology and electronic properties, to probe the factors that control catalysis and electrocatalysis by supported Pt clusters in the <25 atom size range. The stability of the clusters, and how this varies with size under heating, adsorbate exposure, and potential cycling will also be discussed.

8:40am **SS2+AS+HC+NS-TuM3 Role of the Strong Metal Support Interaction on the Catalytic Activity of Platinum Deposited on TiO_2 Supports**, ***R.Paul Hansen,*** *R.S. Phillips,* University at Albany-SUNY; *E.T. Eisenbraun, C.A. Ventrice, Jr.,* SUNY Polytechnic Institute

Several roadblocks prevent the large-scale commercialization of hydrogen fuel cells, including the stability of catalysts and their substrates and the high cost of the Pt involved in the oxygen reduction reaction (ORR). The former of these problems can be solved by replacing the traditional carbon support with a conductive metal oxide such as reduced TiO_2, which will not easily corrode and should result in longer lasting fuel cells. The Pt is necessary in the cathode of the fuel cell to overcome the slow kinetics of the ORR. In this study, Pt was deposited either by atomic layer deposition (ALD) or physical vapor deposition (PVD). The typical size of the Pt islands that were grown using these deposition techniques was 5-8 nm. One factor that can inhibit the catalytic activity of a metal catalyst on a metal oxide is the strong metal support interaction (SMSI). This is where a metal on a reducible metal oxide can be encapsulated by a layer of the metal oxide support material at elevated temperatures. The processing of materials through atomic layer deposition can exceed this temperature. The TiO_2 substrates used in this study were either grown by ALD, which results in a polycrystalline anatase film, or were single-crystal rutile TiO_2(110) samples prepared in ultra-high vacuum (UHV). The Pt/TiO_2 samples were tested electrochemically using cyclic voltammetry (CV) to determine the level of catalytic activity. To determine the effect of the SMSI interaction on the

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

catalytic activity of the PVD grown samples, CV was performed on samples that were annealed in high vacuum after Pt deposition. Additional characterization was performed with scanning electron microscopy (SEM), Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), and four point probe analysis.

9:00am **SS2+AS+HC+NS-TuM4 Adsorption and Adhesion Energies of Au, Cu, and Ag Nanoparticles on CeO_2(111), MgO(100) and Other Oxide Surfaces***, **Charles T. Campbell**, S.L. Hemmingson, G.M. Feeley,* University of Washington

Heterogeneous catalysts consisting of late transition metal nanoparticles dispersed across oxide supports are ubiquitous in industrial chemistry and energy technology. We have used an ultrahigh vacuum single-crystal adsorption calorimeter to study the adsorption energies of Au, Cu and Ag gas atoms as they adsorb and grow nanoparticles on single-crystal oxide surfaces as models for real catalyst systems. These measurements allow us to determine the chemical potential of metal atoms in supported nanoparticles as a function of particle size and the support upon which they sit. The support effect manifests itself very directly on metal chemical potential via the metal / oxide adhesion energy. Our earlier studies have shown that metal chemical potential can be related to the metal nanoparticle's catalytic activity and deactivation rates through sintering, so there is a great motivation to understand how it varies with particle size and support, and how metal / oxide adhesion energies vary with the nature of the metal and the oxide support material. Through these measurements on a variety of systems, we have discovered systematic trends in these that allow predictions of adhesion energies for system which have not been measured. We have also measured the adsorption energy of isolated Cu atoms on CeO_2(111) terrace sites, which is possible at 100 K. This is the first measurement of the adsorption energy of any late transition metal atom on any oxide surface of the type used as catalyst supports in a situation where the atom sits on the surface as an isolated monomer (as opposed to sitting within a small metal cluster).

9:20am **SS2+AS+HC+NS-TuM5 Effects of Nanoparticles on Surface Resistivity: Ni on Au(111)***, **Joshua Cohen**, R.G. Tobin,* Tufts University

The change in surface resistivity due to the formation of nickel nanoparticles on gold(111) was studied by measuring the resistance of a thin film of Au as a function of Ni coverage, θ. After annealing, Au(111) configures into the herringbone reconstruction and provides a template for the periodic nucleation and growth of Ni nanoparticles. The Ni islands grow radially until θ ~ 0.3 ML, after which, subsequent Ni atoms contribute almost exclusively to a second layer [1].

Surface resistivity arises primarily from the scattering of the substrate's conduction electrons by foreign atoms or defects, and studies of the dependence of surface resistivity on coverage yield insights into growth dynamics, interadsorbate interactions, and interactions between the adsorbed atoms and conduction electrons. For randomly distributed non-interacting scatterers the resistivity change is linear in coverage. Since Ni atoms on Au(111) grow in tight ordered nanoclusters, a nonlinear dependence might be anticipated. Our results, however, show a linear dependence on coverage for Ni atoms in the first layer, as if they were independent point scatterers. At coverages above θ ~ 0.3 ML, there is no further change in resistivity, which we attribute to Ni atoms forming a second layer and making no significant contribution to the surface resistivity.

The samples were 150 nm thick epitaxial Au(111) films on mica prepared by sputtering and annealing in ultrahigh vacuum. The resistance of the film was measured as Ni was thermally evaporated on the surface. Ni coverage was determined using Auger electron spectroscopy (AES), corrected for the inelastic mean free path of the electrons.

The resistance and AES data were analyzed in terms of a growth model that allowed for variation in the coverage at which a second layer begins, the relative probabilities of first- and second-layer growth after that point, and the relative contributions of first- and second-layer Ni atoms to the surface resistivity. The results are consistent with the growth model observed with STM [1], and serve as an indirect probe of the growth kinetics of this interesting system, as well as determining for the first time the contributions of the Ni islands to the surface resistivity of the Au film.

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9:40am **SS2+AS+HC+NS-TuM6 Three-Dimensional Control of Nanoparticle Layer Deposition by "Click Chemistry"***, **Mackenzie Williams**, A.V. Teplyakov,* University of Delaware

Our previous studies have focused on the formation of highly-controlled nanoparticle mono- and multilayers of silica and magnetic iron oxide nanoparticles through the copper(I) catalyzed azide-alkyne cycloaddition reaction. By using the specific functionalization scheme in that method, we achieved very high surface coverage and the formation of exactly one nanoparticle layer per deposition cycle, as could be observed with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Formation of the triazole ring from the "click" reaction was confirmed by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS), while density functional theory calculations were used to confirm spectroscopic results and investigate the reasons behind the high coverage. In the current work, a higher level of control over the nanoparticle layers is being sought. Conformal filling of the layer over high aspect-ratio features is being studied and would allow this method to be used as a viable alternative to traditional layer-by-layer techniques. Additionally, control of the spatial resolution of the nanoparticle layers upon the substrate via alternative methods of catalysis initiation is currently being investigated.

11:00am **SS2+AS+HC+NS-TuM10 Spherical Metallic Nanostructures Based on Fullerene Scaffolds with Tunable Bandgap, A Scanning Tunneling Microscopy/Spectroscopy (STM/STS) Study***, **Ehsan Monazami**,* University of Virginia*; J.B. McClimon,* University of Pennsylvania*; J.M. Rondinelli,* Northwestern University*; P. Reinke,* University of Virginia

The current literature on annealing of fullerene molecules on tungsten surfaces indicates a complete dissociation of the fullerene cage and the formation of a carbide phase. However, our measurements with high resolution STM and STS illustrate a complex intermediate reaction sequence. Upon annealing of C_{60} adsorbed on a tungsten thin film grown on MgO (001) in UHV, C_{60} does not dissociate and the spherical C_{60} shape is retained up to a temperature of at least 973 K. During the annealing, the band gap of the molecular layer decreases gradually from the wide bandgap of fullerene to a fully metallic electronic state. This transition occurs in a narrow temperature range between 600 K and 700 K. After this transition, the near-spherical particles are termed "nanospheres." This progression was observed with a series of high resolution scanning tunneling spectra and detailed spectral mapping. The bandgap variation presents an approach to achieve the formation of densely packed nanoclusters (nanospheres) with variable bandgap, which are stable at elevated temperatures. Experimental results for sub-ML fullerene coverage on tungsten show that the fullerene molecules are mobile at room temperature, but they become stationary after annealing above 500 K. This immobilization of molecules indicates a strong interaction and likely a covalent bond between the molecule and substrate that is triggered by annealing.

The progression to metallic nanospheres is hypothesized to occur either by gradual substitution of W-atoms or by wetting the molecule with W-atoms and thus formation of W-C bonds in a solid state reaction. These models were tested using density functional theory (DFT) calculations. Two simulation strategies were used. In the first, C_{60} carbon atoms were substituted by W in the molecule and the resulting electronic properties and bandgap were calculated. In the second approach, different adsorption geometries of a C_{60} molecule on the tungsten (110) surface were considered. The variation of the band gap due to different C_{60} orientations relative to the tungsten substrate and various types of hetero-fullerenes will be discussed.

11:20am **SS2+AS+HC+NS-TuM11 Facile Synthesis of Gold Nanoworms and their Excellent Surface Enhanced Raman Scattering (SERS) and Catalytic Properties***, **Waqqar Ahmed**,* COMSATS Institute of Information Technology, Pakistan*; J.M. van Ruitenbeek,* Leiden University, Netherlands

Gold nanoparticles exhibit interesting optical properties because of the surface plasmon resonance. The shape and size of gold nanoparticles can markedly influence their optical properties. A spherical nanoparticle has a single palsmon peak, while rod-shaped nanoparticles have two plasmon peaks because of their shape anisotropy. Furthermore, slight deviations from the rod morphology can markedly influence the optical properties. For example, worm-shaped gold nanoparticles can have more than two plasmon peaks. Moreover, nanoworms can display very high local field enhancements upon plasmon excitation owing to their special shape and surface roughness.

We have devised a simple, seedless, high-yield protocol for the synthesis of gold nanoworms [1]. Nanoworms were grown simply by reducing $HAuCl_4$

with ascorbic acid in a high pH reaction medium in the presence of growth directional agents. In contrast to the seed-mediated growth of gold nanorods where a seed particle grows into a nanorod, nanoworms grew by oriental attachment of nanoparticles. By varying different reaction parameters we were able to control the length of NWs from a few nanometers to micrometers. Furthermore, the aspect ratio can also be tuned over a wide range.

Owing to their special morphology, gold nanoworms are much superior than the conventional nanorods for numerous applications. For instance, we have seen that they show markedly superior SERS and catalytic properties compared to their nanorod counterparts. This is due to their high-energy rough surface and twisted shape, which not only provides an ideal platform for catalytic activities but also generates local hot-spots upon plasmon excitation. Our study shows that both catalytic and SERS properties of gold nanoworms are strongly dependent on their length.

[1] W. Ahmed, C. Glass, and J.M. van Ruitenbeek, *Nanoscale*, 6, 13222, (2014)

11:40am **SS2+AS+HC+NS-TuM12 Surface Hydrogen Enables Sub-Eutectic Vapor-Liquid-Solid Semiconductor Nanowire Growth***, S.V. Sivaram, H. Hui,* Georgia Institute of Technology*; M. de la Mata, J. Arbiol,* Catalan Institute of Nanoscience and Nanotechnology, Spain*; **Michael Filler**,* Georgia Institute of Technology

Semiconductor nanowires are emerging as indispensable nanoscale building blocks for next generation energy conversion, electronic, and photonic devices. The bottom-up vapor-liquid-solid (VLS) mechanism – whereby a liquid eutectic "catalyst" droplet collects precursor molecules (or atoms) from the vapor and directs crystallization of the solid nanowire – is a nearly ubiquitous method for nanowire synthesis. While VLS growth below the bulk metal-semiconductor eutectic temperature has long been known, the fundamental processes that govern this behavior are poorly understood. Here, we show that hydrogen atoms adsorbed on the Ge nanowire sidewall enable AuGe catalyst supercooling and control Au transport. Our experimental approach combines in situ infrared spectroscopy to directly and quantitatively determine hydrogen atom coverage with a "regrowth" step that allows catalyst phase to be determined with ex situ electron microscopy. Maintenance of a supercooled catalyst with only hydrogen radical delivery confirms the centrality of sidewall chemistry. This work underscores the importance of the nanowire sidewall and its chemistry on catalyst state, identifies new methods to regulate catalyst composition, and provides synthetic strategies for sub-eutectic growth in other nanowire systems. We leverage this newfound understanding of nanowire growth chemistry to fabricate large-area arrays of high quality axial Si/Ge heterostructures for the first time.

12:00pm **SS2+AS+HC+NS-TuM13 Ultrafine Sodium Titanate Nanowires with Extraordinary Strontium Ion-Exchange Property***, **Koji Nakayama**,* Tohoku University, Japan

The removal of radioactive substances released to the environment by a nuclear accident is an emergent issue. The water treatment based on the ion exchange process is the most effective decontamination technology, and inorganic ion exchangers, titanates, have been used for the capture of Sr ions owing to their high radiation stability and extreme ion selectivity. However, the reported adsorption capacity and ion exchange efficiency are not satisfied. We show the formation of sodium titanate nanowires with a few nanometers in diameter, having a mogul-shaped surface, forming hierarchically a three-dimensional network skeletal structure, and exhibiting remarkable Sr ion exchange properties [1]. They are produced by unique and simple non-thermal processes through the simultaneous selective leaching of Al and oxidation of Ti in a rapidly solidified Ti-Al alloy ribbon in NaOH solution. The experimental saturated adsorption capacity is tripledand the uptake rate is at least three hundredtimes faster than these of the previous reports. The results demonstrate that the newly created nanowires exhibit a potential application in the decontamination and disposal of nuclear waste.

[1] Y. Ishikawa, S. Tsukimoto, K. S. Nakayama, and N. Asao, Nano Lett. **15**, 2980-2984 (2015).

Applied Surface Science
Room 101B - Session AS+SS-TuA

Data Analytics in Surface Science and Nanoscience

Moderators: Anders Mikkelsen, Lund University, Sweden, Petra Reinke, University of Virginia

2:20pm **AS+SS-TuA1 Fast Strain Mapping of Nanowire Light-Emitting Diodes Using Nanofocused X-ray Beams***, T. Stankevic,* Copenhagen University, Denmark*; U. Johansson, L. Samuelson,* Lund University, Sweden*; G. Falkenberg,* DESY, Hamburg, Germany*; R. Feidenhans'l,* Copenhagen University, Denmark*; **Anders Mikkelsen,*** Lund University, Sweden

Nanofocused X-ray beams are nondestructive probes that uniquely allow direct measurements of the nanoscale strain distribution and composition found at the interfaces and surfaces inside the micrometer thick layered structures ofmany electronic device architectures [1]. While the method has generally been considered time consuming, we demonstrate that by special design of X-ray nanobeam diffraction experiment we can (in a single 2D scan with no sample rotation) measure the individual strain and composition profiles of many structures in an array of upright standing nanowires[2]. We make use of the observation that in the generic nanowire device configuration, which is found in high-speed transistors, solar cells, and light-emitting diodes, each wire exhibits very small degrees of random tilts and twists toward the substrate. Although the tilt and twist are very small, they give a new contrast mechanism between different wires. In the present case, we image complex nanowires for nanoLED fabrication and compare to theoretical simulations, demonstrating that this fast method is suitable for real nanostructured devices.

We then go on to discuss the complications of data analysis as the amount of data available is dramatically increased with the advent of new highly coherent synchrotrons such as MAX IV in Lund Sweden [3] and improved experimental setups[2,4,5]. Using several detectors that give both real space fluorescence and 2D diffraction information combined with scanning both translational, rotational and time coordinates for in operando and in-situ studies in 3D - an enormous multidimensional dataset can be created in a few days. To fully retrieve all the information inside such dataset and pushing resolution and sensitivity limits new computational methods are needed in combination with advanced modelling.

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[2] T. Stankevic et al, ACS Nano 9 (2015) 6978

[3] " Ultimate upgrade for US synchrotron", Nature 501 (2013) 148

[4] U. Johansson, U. Vogt, A. Mikkelsen, Proc. SPIE 8851, X-Ray Nanoimaging: Instruments and Methods, 88510L (September 26, 2013); doi:10.1117/12.2026609

[5] T. Stankevic et al. Appl. Phys. Lett. 107 (2015) 103101

2:40pm **AS+SS-TuA2 Bellerophon Environment for Analysis of Materials (BEAM), A High Performance Computing Workflow Platform for Materials Research***, E.J. Lingerfelt, A. Belianinov, E. Endeve,* Oak Ridge National Laboratory*; O.S. Ovchinnikov,* Vanderbilt University*; S. Somnath, R.K. Archiblad, S.V. Kalinin, **Stephen Jesse,*** Oak Ridge National Laboratory

Improvements in scientific instrumentation allow imaging at mesoscopic to atomic length scales, many spectroscopic modes, and now—with the rise of multimodal acquisition systems and the associated processing capability—the era of multidimensional, informationally dense data sets has arrived. Technical issues in these combinatorial scientific fields are exacerbated by computational challenges best summarized as a necessity for drastic improvement in the capability to transfer, store, and analyze large volumes of data. The Bellerophon Environment for Analysis of Materials (BEAM) platform provides material scientists the capability to directly leverage the integrated computational and analytical power of High Performance Computing (HPC) to perform scalable data analysis and simulation via an intuitive, cross-platform client user interface. This framework delivers authenticated, "push-button" execution of complex user workflows that deploy data analysis algorithms and computational simulations in HPC environments like Titan at the Oak Ridge Leadership Computing Facility (OLCF).

Here, we address the underlying HPC needs for characterization in the material science community, elaborate how BEAM's design and infrastructure tackle those needs, and present a small sub-set of user cases where scientists utilized BEAM across a broad range of analytical techniques and analysis modes. BEAM system will be demonstrated for 4D Ronchigram analysis and property extraction of atomically resolved STEM (Scanning Transmission Electron Microscopy) data, parallel spectroscopic curve fitting in SPM (Scanning Probe Microscopy) data, and image segmentation.

Acknowledgements

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3:00pm **AS+SS-TuA3 The Center for Advanced Methods for Energy Research Applications (CAMERA):Mathematical Methods for Data Science from Experimental Facilities***, **James Sethian,*** University of California at Berkeley **INVITED**

The Center for Advanced Methods for Energy Research Applications (CAMERA), jointly funded by the U.S. Department of Energy Offices of Advanced Scientific Research (ASCR) and Basic Energy Sciences (BES), focuses on mathematical models, algorithms, and codes thatanalyze, interpret, and understand the information contained within experimental data, particularly arising from light sources and nanoscale facilities. Initial focus areas include ptychography, tomography, grazing incidence small-angle scattering, image analysis and reconstruction methods, fluctuation scattering, single particle imaging, fast electronic structure methods, and automatic materials characterization and design. In this talk, we will describe the structure of CAMERA, and summarize some of the major projects. In particular, we will discuss work on: (1) Algorithms for real-time streaming ptychography. Ptychographical phase retrieval is a non-linear optimization problem, made tractable through exploiting redundancy inherent in obtaining diffraction patterns from overlapping regions of the sample. Here, we describe SHARP: our "Scalable Hetereogeneous Adaptive Real-time Ptychography" framework that enables high-throughput streaming analysis. (2) New algorithms for fluctuation scattering and single particle imaging: In single particle diffraction (SPD) imaging, a large number of X-ray diffraction images are collected from individual particles, which are delivered to an ultrabright X-ray beam at random and unknown orientations through either a liquid droplet or aerosol delivery system. Recently, a new mathematical and algorithmic procedure has been introduced, known as "Multi-tiered Iterative Phasing" (MTIP), which simultaneously determines the orientations, 3D intensity function, complex phases, and the underlying molecular structure together in a single iterative process. (3) Machine learning methods for classification and characterization of scattering patterns. Grazing Incidence Small Angle X-ray Scattering (GISAXS) is an important reciprocal-space imaging modality which provides statistical information about a sample in 3-D. GISAXS is widely used for studying thin films that play a vital role as building blocks for the next generation of renewable energy technology. One challenge in GISAXS imaging is to be able to accurately infer properties of the material such as the crystal lattice corresponding to the sample from a single 2-D diffraction/scatter patterns. We will discuss our work using machine learning algorithms and convolution neural net classifiers to automatically provide structural details about the sample by analyzing the measured GISAXS diffraction patterns.

4:20pm **AS+SS-TuA7 New Data Analysis Tools for X-ray Photoelectron Spectroscopy (XPS) and Spectroscopic Ellipsometry (SE)***, **Matthew Linford,** B. Singh, J. Bagley,* Brigham Young University*; J. Terry,* Illinois Institute of Technology*; A. Herrera-Gomez,* CINVESTAV-Unidad, Mexico

Here we discuss a series of new data analysis tools for X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry (SE). For XPS, these include uniqueness plots, and the equivalent and autocorrelation widths. For SE, they include distance, principal component, and cluster analyses. Uniqueness plots are widely used in the SE community for identifying correlation between fit parameters. They are easily interpreted. However, they appear not to have been employed for XPS data analysis. And certainly better tools are needed to identify inappropriate peak fits to XPS narrow scans because (i) XPS is now receiving in excess of 10,000 mentions in the literature each year, and (ii) with the proliferation of the technique, the number of untrained users that are collecting and fitting data has significantly increased. In a number of reported peak fits, too many fit parameters have been introduced into the data modeling, which has reduced or eliminated the statistical meaning of these parameters. Uniqueness plots show the error of a fit as a function of one of the variables in that fit, where the values of a specified variable are systematically fixed to quantities about its optimal value. If the same, low error can be obtained for all the values of the variable in question, a horizontal line is obtained, which signals fit parameter correlation. Here, the same error is obtained because other variables in the fit can compensate for the systematic change to the variable in question. In contrast, if the error in the fit rises as the variable in question is systematically changed about its optimal value, the fit has uniqueness. Uniqueness plots that indicate the absence of fit parameter correlation are often parabolic in shape. We have applied uniqueness plots to the peak fitting of XPS C 1s narrow scans of ozone-treated carbon nanotube (CNT) forests that were obtained as part of a study on CNT-templated thin layer chromatography plates, and Si 2p narrow scans of oxidized silicon. In both cases, uniqueness plots showed that unconstrained fits had poor uniqueness, while more reasonably constrained fits had better uniqueness. These results indicate that uniqueness plots may be a valuable tool for identifying inappropriate peak fits in XPS. In this presentation, I will also briefly mention the use of the equivalent and autocorrelation widths in analyzing XPS narrow scans, and then focus on distance, principal component, and cluster analyses in SE data analysis. Our recent (2016) paper on this topic appears to be only the second example of the application of chemometrics to SE data analysis in the literature.

4:40pm **AS+SS-TuA8 A Surface Investigation of Parchments using ToF-SIMS and Principle Component Analysis***, **Marie-Laure Abel**, J.F. Watts, V. Vilde,* University of Surrey, UK

Parchments are an historical writing support mostly used during the Middle Ages. Their popularity dates from the second century before Christ (BC) in Pergame, Turkey, from which the name originates. Unlike paper, parchment is made of animal skin with a process similar to that used to produce leather. The products used in the fabrication vary and any animal species can be used, although most historical parchments are made from sheep, goat and calf. Information of species recognition on parchments is currently provided either using proteomics or DNA analysis. However each technique presents difficulties and sometimes it is not possible to obtain an unambiguous result. Many valuables manuscripts are written on parchment such as the Magna Carta or the Codex Sinaiticus, which justifies the effort put towards the study of this material in order to improve the conservation process and to learn more about its history.

In this work, a new technique was used in order to assess if any information may be gleaned and help in the process of recognition or even providing any further information to conservators to be used for preservation of historical parchment. Time of flight secondary ion mass spectrometry (ToF-SIMS) has been applied to the analysis of parchment specimens. Indeed while ToF-SIMS has been previously applied to a variety of samples of some significance in the cultural heritage field such as paintings or mummies, it has not been applied to parchments. To facilitate the data treatment process, this has been coupled with data analysis using chemometrics, namely principle component analysis (PCA).

A series of specimens of various ages and species were analysed on both sides, "skin" and "flesh". These samples included sheep, goat and calf. In addition, an unknown sample was also introduced to ascertain if its characteristics could be shown to be close to any species. Results indicate that it is fairly straightforward to distinguish between goat and sheep while calf is more difficult to separate from other species which is unexpected as biologically goat and sheep are considered the closest species within the selection. Furthermore the unknown specimen exhibits data which would classify it as a goat specimen. Considering the sides examined separations are seen within one particular species but the direction of the variation is not the same from one species to another. More work is needed to ascertain which side is being analysed for any unknown materials as the behaviour varies amongst the species examined in this work.

5:00pm **AS+SS-TuA9 Multivariate Analysis of Very Large Hyperspectral SIMS Datasets: What Can We Do, and What Would We Like to Do?***, **Henrik Arlinghaus**,* ION-TOF GmbH, Germany **INVITED**

Advances in instrumentation capabilities, as well as increases in the complexity of modern materials have resulted in a corresponding increase in the size and complexity of data acquired during sample analysis. The increase in the spatial and spectral resolution of the instrumentation is nominally a boon to the analyst, as the measured data more accurately depicts the sample. However, the resulting hyperspectral images routinely consist of upwards of ten thousand pixel spectra for 2D analyses (e.g. a 128x128 pixel image), or millions of voxel spectra for 3D analyses, each of which may consist of hundreds or thousands of ion peaks. Because of the sheer amount of information contained within such an image, it is often no longer feasible to conduct a full manual analysis of the data. An additional factor exacerbating this issue is the fact that many studies necessitate the analysis of a series of spatially resolved replicate measurements of a single sample, or of multiple similar samples. In these studies the aim is not only to characterize the contents of each individual measurement, but also to determine the similarities and differences between the measurements, while ignoring subtle differences caused by changes in analysis conditions between the individual measurements.

A solution to the problem of information overload is the use of multivariate analysis techniques to help guide the analyst, in order to reduce the time needed for determining the chemical make-up of the analyzed samples. These techniques use different approaches in order to reduce the dimensionality of the measured data, resulting in a small set of factors which recreate a simplified model of the data.

The use of MVA approaches, such as Principal Component Analysis (PCA) and Maximum Autocorrelation Factors (MAF), has become an established method of simplifying the analysis of SIMS data arising from a single measurement. We will discuss alternatives to these commonly used methods, including new variations of Multivariate Curve Resolution (MCR) which use additional optimization criteria, as well as MVA approaches not commonly used in SIMS data analysis. Additionally, we will discuss the unique challenges which may arise when applying MVA techniques to the full hyperspectral data contents of a series of measurements.

5:40pm **AS+SS-TuA11 High mass-resolution 3D ToF-SIMS: PCA and visualization in seconds using Graphical Processor Units (GPUs)***, **Peter Cumpson**, I.W. Fletcher, N. Sano, A.J. Barlow,* Newcastle University, UK

Multivariate analysis offers the exciting prospect of unlocking the information content of 3D SIMS of complex organic and biological samples with sub-micron resolution. However applying principal component analysis (PCA) to large images or 3D imaging depth-profiles has been difficult until now because of the Gb to Tb size of the matrices of data involved. The result has always been an "out of memory" error.

Recently[1] we applied two algorithms, RV1 and RV2, originally developed by Halko *et al*[2] that improve the speed of PCA and allow datasets of unlimited size respectively, even on ordinary personal computers. In this presentation we show results of applying these algorithms to perform PCA on full 3D ToF-SIMS data of several examples of plant and small animal tissue. The datasets we process in this way are typically 128x128 or 256x256 pixel depth-profiles of around 100 layers, each voxel having a 70,000 value mass spectrum associated with it, giving datasets of at least 1Tb in size when uncompressed. These data were acquired using our Ionoptika J105 and Iontof IV instruments, with Helium Ion Microscope images of particular key features.

Even for such large datasets a rapid PCA calculation is often needed during analysis sessions to inform decisions on the next analytical step. We have therefore implemented the RV1 algorithm on a PC having a Graphical Processor Unit (GPU) card containing 2,880 individual processor cores[3]. This increases the speed of calculation by a factor of around 4 compared to what is possible using the fastest commercially-available desktop PCs, and full PCA is now performed in less than 7 seconds.

We then use the GPU to allow real-time interactive visualization of the principal components in 3D. This leads to some spectacular and information-rich tomographic images that can be an excellent basis for discussion between analysts and the biologists and medics who understand the morphology and anatomy of their tissue samples.

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[2] N P Halko et al, *SIAM Review,Survey Rev. Sec.* 53 (2011) 217–288.

[3] P J Cumpson et al, *Surf. and Interface Anal*., onlinelibrary.wiley.com/doi/10.1002/sia.6042/full

6:00pm **AS+SS-TuA12 Mass Spectrometry Image Fusion***, **Bonnie June Tyler**,* Universität Münster, Germany*; H.F. Arlinghaus,* University of Muenster, Germany

As mass spectrometry imaging (MSI) has moved from the technique development stage into real world biological studies, the need to combine mass spectrometry images with other biologically relevant imaging techniques has become important. Techniques as diverse as electron microscopy, scanning probe microscopy, XPS imaging, H&E staining, and fluorescent labeling can provide important information that is complementary to the mass spectral images. Combining the information from these complementary measurements is often necessary for accurate understanding of biological samples. Within the field of mass spectrometry imaging alone, combining different imaging modes, such as MALDI/ToF-SIMS, or GCIB ToF-SIMS/LMIG ToF-SIMS, can enhance understanding of the specimens being studied.

In theory, more data should enable more confident conclusions. In practice, however, the challenges of handling and reducing very large imaging data sets, that have disparities in spatial resolution and contrast mechanisms, can result in biased or misleading conclusions. In order to facilitate more consistent, accurate and useful descriptions of real world samples, advanced data exploration tools are needed. Image fusion is an approach to combining data from different sources that is receiving increasing attention within the field of mass spectrometry imaging.

Although many algorithms for image fusion have been developed for applications in remote sensing, medical imaging and photography, the distinctive features of mass spectrometry make many of these techniques inappropriate for use in this field. We have tested algorithms from two major classes of image fusion, those that operate in the spatial domain and those that operate in the frequency domain. Common artefacts caused by the different algorithms have been identified. Two modified algorithms have been developed which can be used to produce satisfactory fused images using mass spectrometry data. The first approach combines multivariate analysis (MVA) and discreet cosine transform (DCT) and is useful for combining MSI images with monochromatic images. The second algorithm, which uses a combination of multivariate methods, is useful for fusing MSI data with a second spectral image. Both of these new image fusion approaches have been tested on simulations, model systems and real tissue samples. We have shown that MVA image fusion can be a valuable technique for reducing noise, improving image contrast and enhancing the sharpness of mass spectrometry images. With appropriate attention to the distinctive features of each imaging method, image fusion can be done without significant artefacts or distortion of the spectral detail.

Biomaterial Interfaces
Room 101A - Session BI+AS+SA-TuA
Biophysics and Characterization of Biological and Biomaterial Surfaces

Moderators: Eva Chi, University of New Mexico, Axel Rosenhahn, Ruhr-University Bochum, Germany

2:20pm **BI+AS+SA-TuA1 Resolving Non-specific and Specific Adhesive Interactions of Catechols at Solid/Liquid Interfaces at the Single Molecular Scale***, T. Utzig,* Max-Planck Institut für Eisenforschung GmbH, Germany*; P. Stock,* Max Planck Institut fur Eisenforschung GmbH, Germany*; **Markus Valtiner**,* Technische Universität Freiberg, Germany

The adhesive system of mussels evolved into a powerful and adaptive system with affinity to a wide range of surfaces. It is widely known that thereby 3,4-dihydroxyphenylalanine (Dopa) plays a central role. However underlying binding energies remain unknown at the single molecular scale. Here, we use single molecule force spectroscopy to estimate binding energies and binding mechanism of single catechols with a large range of opposing chemical functionalities. Our data demonstrates significant interactions of Dopa with all functionalities, yet most interactions fall within the medium-strong range of 10-20 k_BT. Specifically, Dopa-molecules interact with surfaces exposing different functionalities via different types of interactions ranging from bidentate H-bonding plus metal coordination (titania), monodentate H-bonding (SAMs exposing H-donor or H-acceptor headgroups), the hydrophobic interaction (alkyl SAM) or interactions involving the p-electron system of Dopa's catechol ring (gold). Only bi-dentate binding to TiO_2 surfaces exhibits a higher binding energy of 29 k_BT. Our data also demonstrates at the single molecule level that oxidized Dopa and amines exhibit interaction energies in the range of covalent bonds, confirming the important role of Dopa for cross-linking in the bulk mussel adhesive. We anticipate that our approach and data will further advance the understanding of biologic and technologic adhesives.

2:40pm **BI+AS+SA-TuA2 Protein-Nanoparticles Interactions: Surface Chemistry, Protein Corona and Secondary Structural Changes***, I. Ojea, R. Capomaccio, L. Calzolai, D. Gilliland, P. Colpo, **Giacomo Ceccone**,* EC-JRC-IHCP, Italy*; G. Siligardi, R. Hussein,* Diamond Light Source, Oxfordshire, UK

The characterisation of protein corona formed around nanoparticles is a very important and challenging issue in the investigation of nanomaterials behaviour in biological environment and has been studied by many authors [1, 2, 3,4].

On the other hand, it is recognized that detailed physico-chemical characterization of nanomaterials is becoming increasingly important both from the technological and from health and safety point of view. Moreover, an incomplete characterisation may inhibit or delay the scientific and technological impact of nanoscience and nanotechnology [5]. In this respect, surface chemical analysis methods, such as X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry, can provide an important contribution to more fully characterizing nanomaterials [6].

In this work, we have investigated the interaction of human serum albumin (HSA) with gold nanoparticles (AuNPs) functionalized with thiols. In particular, 15 nm AuNPs functionalized with PEG thiols have been studied before and after interaction with HSA.

The different steps of sample preparation have been characterised by DLS, CPS and TEM, whilst the surface chemistry has been mainly assessed by XPS. Finally, the interaction between nanoparticles and HSA has been studied by Synchrotron Radiation Circular Dichroism (SRCD) to gather information on the protein structure [7]. In particular, XPS and ToF-SIMS data revealed the presence of HSA on pegylated nanoparticles, whilst the use of SRCD in combination with separation techniques allowed the determination of the structure and morphology of HSA-AuNPs complexes [8]. Moreover, SRCD experiments indicate that AuNPs increase the UV and thermal stability of HSA.

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3:00pm **BI+AS+SA-TuA3 Measuring the Impact of the Surface of Protein Stability using Single Molecule Experiments with the AFM***, **Phil Williams**, S. Allen, A. Oyefeso, G. Milson, E. Fornari,* University of Nottingham, UK **INVITED**

Seven out of the top eight top-selling medicines of 2014 were biological in origin (so-called biopharmaceuticals or biologics). Successful formulation of such biopharmaceuticals has created new challenges to the pharmaceutical industry since the physical and chemical properties of the biological molecule (protein, peptide, RNA, DNA) differ from those of small 'classical drug' molecules. Whilst single molecule force spectroscopy has given new insight to many ligand/receptor interactions, the requirement to chemically functionalize the surfaces of both the substrate and the tip render the technique of little interest to the pharmaceutical industry since such functionalization, by definition, changes the chemistry of the ligand and receptor. Furthermore, this experimental methodology precludes effective screening of agents binding to a target receptor.

I will highlight our development of a fragment screening methodology using the AFM for single molecule force measurements without chemical modification of the ligands. I will introduce the method validating its approach using the streptavidin/biotin system that is often used as a model. I will then demonstrate the potential of the methodology to find fragments that interact with thrombin, a target for cardiovascular disease therapy.

In developing the above approach, it became apparent that actually neither the tip nor the substrate needs to be functionalized. I will conclude by discussing a promising method to screen for excipients that may stabilize protein structure in formulation and storage, where no chemical functionalization is necessary. The technique permits the measurement of the stability of proteins to be measured through their susceptibility to denaturants, such as urea and guanidinium chloride, and the effect of excipients on the measured stability to be assessed. For some proteins, the stability measured through traditional bulk methods, such as fluorescence, match those measured using the AFM, whereas for others there appears to be a significant difference. I propose, therefore, that this AFM method offers an interesting way to study protein denaturation at an interface.

4:20pm **BI+AS+SA-TuA7 In Vitro Characterization of Interfaces for the Development of Antibacterial and Biocompatible Surfaces*, Katharina Maniura,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

Cell culture and bacterial studies of novel materials and new functional surfaces often show very poor correlation with clinical outcomes. This fact not only poses a major challenge for basic and industrial researchers, it is also associated with high costs.

Generally, the majority of biomaterials are tested using *in vitro* cell monocultures, however, this approach neglects possible synergistic interactions between different cell types and paracrine signalling mediating the tissue-specific response to a material.

Immediately upon implantation, medical implants get exposed to the patient's blood and this initiates the first phase of wound healing and subsequent cell recruitment and response deciding about material integration or non-integration.

We have established that blood pre-incubation of implant surfaces mimics a more physiological situation, providing a more predictive *in vitro* model for the evaluation of novel implant surfaces.

Similarly, many promising antimicrobial materials failed to make the translation from bench to bedside, partially due to insufficient *in vitro* biofilm models used for predicting the long-term *in vivo* antimicrobial and anti-biofilm activity. For the evaluation of novel surfaces the actual forseen implantation location and its biological environment need be considered to design a more predictive bacterial study with conditions mimicking the *in vivo* situation.

5:00pm **BI+AS+SA-TuA9 Vibrational Sum-Frequency Scattering Spectroscopy for Characterization of Biomaterial Interfaces in Biological Environments*, Patrik Johansson,*** *C. McDonald, Y.-C. Wang, P. Koelsch, D.G. Castner,* University of Washington

Most biomaterials have a 3-dimensional structure, of which the interfacial properties play an essential role in their interactions with biomolecules in the surrounding environment. The dynamics of protein adsorption onto biomaterials, and the induced conformational changes or selective orientations following such interactions, are phenomena that to a large extent govern the biocompatibility of such materials. However, direct measurement of these interactions in biological environments are challenging as most techniques often (1) lack interfacial specificity, (2) require model samples with inherent limitations, or (3) lack specificity for the chemistry, orientation, and conformation of the probed species. In this work, we demonstrate how vibrational sum-frequency scattering (SFS) can be used to provide all this information, without the use of labels, from biomolecules specifically at the surface of biomaterials in biological environments.

We first show that SFS can yield chemical information via vibrational spectra selectively from molecules used to functionalize the surface of nanoparticles. Spectral changes upon addition of proteins to the samples do not only confirm adsorption onto the nanoparticles, but also provide information about the secondary conformation for the adsorbed proteins. It is likely that continuous development of SFS will make it an essential tool for evaluating the biocompatibility and other properties of nanoparticles for use in biomedical applications.

We have also applied SFS on protein fibers, for which a detailed understanding of the structure, function, interactions, conformation, and dynamics is critical for refining strategies in tissue engineering, as well as for the development of treatments for progressive diseases involving protein fibers, such as Alzheimer's disease (AD). In our studies, we have found that collagen fibers assembled *in vitro* exhibit a very large SFS cross-section, and that the spectral signatures are dependent on the scattering angle, implying that this parameter can be adjusted to selectively study specific features of the fibers. Data analysis routines, including maximum entropy method calculations, reveal the relative phase of various chemical groups in the fibers, which can be utilized for determining their relative orientations.

Finally, we have demonstrated that amyloid fibers and spherulites, which are structures found in the brain tissue of patients with AD, exhibit strong nonlinear optical properties. We believe that SFS can reveal new details about the development and interactions of these structures, which can provide clues about AD pathology and help finding new biomarkers for the disease.

5:20pm **BI+AS+SA-TuA10 Imaging ToF-SIMS of Human Breast Cancer Tissues: Connecting Chemical Images to Biology*, Blake Bluestein,*** University of Washington*; F. Morrish, D. Hockenbery,* Fred Hutchinson Cancer Research Center*; L.J. Gamble,* University of Washington

Breast cancer, the most common cancer among women, is known to vary in responsiveness to chemotherapy. Therefore, the role of changes in tumor metabolism affecting the response to chemotherapy is under scrutiny. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) provides a powerful approach to attain spatially-resolved molecular data from cancerous tissues. We use imaging ToF-SIMS and principal components analysis (PCA) to study human biopsy tissue samples to clarify links between fatty acid composition within and around tumors and the potential drug resistance of these tumors. An important component of this project is ToF-SIMS analysis of pre and post neoadjuvant frozen patient specimens. Since treatment occurs with the tumor in place, analysis of biopsies taken pre- and post-treatment allows characterization of molecular changes in tumors as a response to treatment. Two sets of pre and post chemotherapeutic treated tissue have been studied. Additionally, 11 triple negative (TN) pre-treatment tissues have been studied using PCA to determine if molecular differences within tumor tissues can be correlated with patient response to treatment.

Data were acquired with an IONTOF TOF.SIMS V using a Bi_3^+ analysis beam. Multiple 1mm^2 areas per tissue section were analyzed by stitching together 25 200µm^2 raster area scans. Data was acquired in both positive and negative polarities. Scores images generated by imaging PCA correlated with cellular and stromal areas were then used as masks to select regions of interest (ROI) that were reconstructed with ToF-SIMS software. Reconstructed spectral data of cellular and stromal areas was subsequently analyzed using PCA to ascertain molecular differences between tumor tissues.

Utilizing ROIs to select specific regions within analysis areas followed by spectral PCA for two different sets of pre and post treatment tumor biopsies showed a near distinctive chemical separation between pre and post. Chemical differences observed between the pre and post treatment tissue biopsies were related to changes in fatty acids, monoacylglycerols, diacylglycerols and cholesterol. Pretreatment samples showed higher loadings for vitamin E and C18:1 while post treatment samples had higher loadings for sphingomyelin and saturated fatty acids (stearic acid and palmitic acid). Spectral PCA of cellular and stromal region data from the 11 TN tissues separates patients that respond to chemotherapy and those that do not. Patients that respond to chemotherapy show higher loadings of sphingomyelin and saturated fatty acids, while nonresponding patients correlate with loadings of cholesterol, C18:1 and C18:2.

5:40pm **BI+AS+SA-TuA11 Some of These Images are Just Like the Others: Finding Similar Images in Imaging Mass Spectrometry Data Sets*, Daniel Graham,*** *L.J. Gamble,* University of Washington

Mass spectrometry imaging (MSI) has been applied to many areas of research due to the rich chemical information it can provide. However, MSI also brings a set of challenges due to the enormous size of the data sets. Most modern imaging mass spectrometers produce data that consists of a full mass spectrum at every pixel of each image. This data set can be analyzed either as a series of spectra from a given area of the image, or as a series of images from a given set of peak masses. When looking at a series images, it is of interest to find all masses that have the same spatial distribution since this could provide information about the chemical differences seen throughout a sample, and identify fragments that originate from the same molecules or that co-localize within the analyzed area. In this presentation we demonstrate a simple, useful tool we have developed to process mass spectrometry images and identify which peaks show similar spatial patterns. For this we have created the 'Correlated Image Finder' as part of our NBtoolbox for multivariate analysis of mass spectrometry imaging data. This tool uses one of two methods to find similar images. The first method calculates the correlation coefficient between the pixels of each image and sorts the images according to a user chosen correlation cutoff. The second method uses a simple image subtraction method to find images that match within a user chosen cutoff. For either method, the images are first down binned to reduce image noise and then thresholded and scaled in order to compare all peak images on an equal scale.

The Correlated Image Finder has been tested on a wide variety of images. Examples will be shown from ToF-SIMS and MALDI imaging data. It was seen that the Correlated Image Finder is able to find images showing similar spatial distributions. The Correlated Image Finder can be used on any set of image data and examples will be shown from both 2D and 3D image data sets from tissues, cells and polymers. The results from the Correlated Image Finder can help simplify MSI data interpretation and can also help understand trends seen using other analysis methods such as principal component analysis.

Novel Trends in Synchrotron and FEL-Based Analysis Focus Topic
Room 103C - Session SA+AS+BI+MI-TuA

Synchrotron and XFEL Advances for Biological Systems (2:20-3:40 pm)/Synchrotron Radiation at the Frontiers of Device Technology (4:20-6:20 pm)

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Olivier Renault, CEA-University Grenoble Alps, France

2:20pm **SA+AS+BI+MI-TuA1 Crystal Growth Mechanisms of Biominerals Revealed by Polarization-dependent Imaging Contrast (PIC) Mapping*, Pupa Gilbert,*** University of Wisconsin - Madison **INVITED**

X-ray linear dichroism was first shown in natural biominerals by Metzler et al. [1]. Based on this effect, we developed Polarization-dependent Imaging Contrast (PIC)-mapping, which displayed non-quantitative crystal orientation at the nanoscale as gray levels in ratios of images acquired at different linear polarizations [2]. A later development provided grayscale, semi-quantitative PIC-maps by acquiring stacks of 19 images as the linear polarization was rotated in 5° intervals from 0° to 90° [3-7]. The latest development uses the same stacks of images to fully, quantitatively display crystal orientations in colors, including hue and brightness, which represent in-plane and off-plane crystallographic c-axis orientation angles [8-10].

Using PIC-mapping in these 3 subsequent modes, we discovered several biomineral formation mechanisms in nacre [11,7], sea urchin teeth [12-14], ascidian spicules [10], corals, eggshells, modern and fossil sea shell ultrastructure [15].

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3:00pm **SA+AS+BI+MI-TuA3 New Dimensions in Synchrotron IR Spectroscopy*, Michael Martin,*** Lawrence Berkeley National Laboratory **INVITED**

Synchrotron infrared beamlines use the diffraction-limited beam properties to enable a variety of cutting edge science - how can we go further?

By combining scattering-scanning near-field optical microscopy (s-SNOM) with mid-infrared synchrotron radiation, synchrotron infrared nano-spectroscopy (SINS) enables molecular and phonon vibrational spectroscopic imaging, with rapid spectral acquisition, spanning the full mid-infrared (500-5000 cm^{-1}) region with nanoscale spatial resolution. This highly powerful combination provides access to a qualitatively new form of nano-chemometric analysis with the investigation of nanoscale, mesoscale, and surface phenomena that were previously impossible to study with IR techniques. We have installed a SINS end-station at Beamline 5.4 at the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory, making the s-SNOM technique widely available to non-experts, such that it can be broadly applied to biological, surface chemistry, materials, or environmental science problems. We demonstrate the performance of synchrotron infrared nano-spectroscopy (SINS) on semiconductor, biomineral and protein nanostructures, providing vibrational chemical imaging with sub-zeptomole sensitivity.

The spatial field localization at the tip apex can also result in a large near-field momentum sufficient to optically excite phonon polaritons (PhPs), which are quasiparticles resulting from the strong coupling of photons with optical phonons. Here, we use SINS to image the PhP spectral response in thin hexagonal boron nitride (hBN) crystals. The large spectral bandwidth of the synchrotron source enables the simultaneous measurement of both the out-of-plane (780 cm-1) and in-plane (1370 cm-1) hBN phonon modes. In contrast to the strong and dispersive in-plane mode, the out-of-plane mode PhP response is weak. Measurements of the PhP wavelength reveal a proportional dependence on sample thickness for thin hBN flakes [2].

This talk will present the novel SINS instrumentation and a variety of scientific examples. Future directions, both technical and scientific, will be discussed.

*With Hans A Bechtel, Markus B. Raschke, Z. Shi, F. Wang, R.W. Johns, D.J. Miliron, E.A. Muller, R.L. Olmon

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4:20pm **SA+AS+BI+MI-TuA7 Sample Delivery Methods for X-ray Free Electron Lasers*, Uwe Weierstall,*** Arizona State University **INVITED**

Serial crystallography at XFEL's has shown great promise in recent years for solving crystal structures of proteins, which produce only micron sized crystals. Liquid jets have been very successful for delivery of microcrystals to the X-ray beam. The commonly used liquid injection system will be discussed. High sample consumption has motivated the development of an injector, which uses high viscosity media like Lipidic Cubic Phase (LCP). G-protein coupled receptors are an important group of membrane proteins which are often crystallized in LCP. The injector generations a microscopic stream of LCP with adjustable speed for sample delivery to the X-ray beam[1]. Some important GPCR structures could be solved with this device at the LCLS[2]. In addition, new media with similar viscosity to LCP have been developed which enable delivery of soluble or membrane proteins into the X-ray beam with low sample consumption[3]. The high viscosity injection method has also been shown to facilitate serial diffraction experiments with microcrystals at synchrotron microfocus beamlines. This talk will highlight these developments and discuss the possibilities.

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5:00pm **SA+AS+BI+MI-TuA9 Synchrotron-based Spectroscopy Investigation for Electronic Phase Transition at Highly-Charged Electric-Double-Layer Interfaces***, **Hongtao Yuan**,* SLAC National Accelerator Laboratory **INVITED**

Electric-field control of charge carrier density has attracted much attention since it is remarkably simple for modulating physical properties of condensed matters and for exploring new functionalities with a transistor configuration. Owing to the limitation of dielectric breakdown in most solid dielectrics, the maximum carrier density accumulated in conventional field-effect transistors (FETs) is quite low (<< 10^{13} cm^{-2}) and thus seriously limits the tunability of electronic states of solids, for example, not sufficient enough to induce insulator-to-superconductor transition. While the electric-double-layer transistor (EDLT) with ionic liquids (ILs, or ionic gel) as gate dielectrics have been proved to be able to effectively attain a high carrier density up to levels of around 10^{15} cm^{-2} and to realize a large local electric field up to 50 MV/cm at liquid/solid interfaces. For example, electric-double-layer transistors have been demonstrated for an electric-field control of emergent interfacial quantum phenomena and the electronics phase transitions in condense matters, such as insulator-superconductivity and paramagnetism-ferromagnetism transitions. However, the mechanistic/spectropic understanding of the local electronic structures at such highly charged IL/oxide EDL interfaces and also further modification under gate-bias remain elucidated and challenging.

In this talk, we conducted synchrotron radiation based X-ray absorption spectroscopy (XAS) and Auger electron spectroscopy (AES) combined with in situ electrical measurements to directly characterize the evolution of the electronic structure at a representative IL/$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin film interface. We find a significant valence reduction localized to the topmost LSMO layer after interface formation, and that the gate-bias predominantly modulates this surface reduced Mn species effectively converting these top layers into an insulator. We expect the synchrotron radiation based photon science probing techniques will directly shed light on the understanding of interfacial electronic phase control under the electric field.

(This work was done in collaboration with Bongju Kim, Jun-Sik Lee, Yasuyuki Hikita adn Harold Y. Hwang. This work was supported by the Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under contract DE-AC02-76SF00515.)

5:40pm **SA+AS+BI+MI-TuA11 Correlation of the Conductivity/Magnetic Properties and the Electronic, Crystalline and Compositional Structure of Strongly Correlated Complex-oxide Interfaces and Thin Films***, **Juan Rubio-Zuazo**,* SpLine CRG Beamline at the ESRF The European Synchrotron, France*; G.R. Castro,* SpLIne CRG Beamline at the ESRF The European Synchrotron, France

We study the structural and electronic properties of strongly correlated complex-oxide thin films and interfaces using Hard X-ray Photoelectron Spectroscopy (HAXPES), Electron Energy Loss Spectroscopy (EELS) and Grazing Incidence X-ray diffraction (GIXRD) at the BM25-SpLine beamline (Branch B) at the ESRF. Strongly correlated complex-oxide exhibit a wide variety of interesting physical properties which originate from mutual coupling among spin, charge and lattice degrees of freedom. Usually, the interface drives the magnetic and electric response of the heterostructure. The chemical, mechanical, electric and magnetic properties of such devices are often intimately related to the structure, composition profile and morphology of their surface and internal interfaces. Several mechanisms are present at these interfaces as crystallographic space group modification, presence of oxygen vacancies, dislocations due to lattice strain, deviation from stoichiometry, phase segregation. In general all these phenomena modify the intrinsic properties of the materials used at the heterostructure, offering a unique way to produce artificial correlated materials with tailored properties. The growth of these materials in thin film form opens possibilities for magneto-electronic and spintronic devices applications. The results shown here are focused on the study of the influence of buried interfaces on the electric and magnetic properties of CMR and multiferroics systems. We will show the experimental methodologies at SpLine based on synchrotron radiation techniques to gain quantitative knowledge on the crystallographic and electronic properties at the interface between different complex oxides. There are few techniques able to provide an accurate insight of what is happening at these buried interfaces which in general are buried by several tens of nanometres in the material. The simultaneous combination of hard and soft X-ray photoelectron spectroscopy, electron energy loss spectroscopy with surface/interface X-ray diffraction gives unique capabilities in this respect. Here we will present a series of example to show how the interface properties can change the magnetic-conductivity properties.

6:00pm **SA+AS+BI+MI-TuA12 Interface Passivation of III-V/High-k Materials by High Energy X-ray Photoelectron Spectroscopy: A Quantitative Evaluation***, **Thierry Conard**, V. Spampinato, L. Nyns, S. Sioncke,* IMEC, Belgium*; J.M. Ablett,* Synchrotron SOLEIL- Ligne GALAXIES, France*; W. Vandervorst,* IMEC, KU Leuven, Belgium

The use of InGaAs as a high carrier mobility CMOS-channel material requires a proper electrical passivation of its interface with the gate dielectric. One of the passivation schemes investigated involves the use of Sulphur. In this work, high-k stacks on Sulphur passivated InGaAs substrates involving both Al2O3 and HfO2 are investigated. A major question related to the use of Sulphur relates to the chemical states at the interfaces. XPS is traditionally an important technique for interface analysis but faces several challenges in its application to the above mentioned stacks. First, due to the large number of elements involved, numerous peak interferences are present limiting the choice of useful photoemission peaks. Second, relevant stacks have total thicknesses of the order of 4 nm, which lead to very low intensities , certainly for minority elements like Sulfur. In this work, we discuss the impact of the H_2S passivation temperature as well as the use of TMA pre-pulses in the growth of Al_2O_3. We show that the Sulphur bind to In but that no As-S or Ga-S bonds could be detected. The use of a TMA pre-pulse after surface passivation leads to a reduction of the amount of Sulphur present at the interface and likely increases the amount of In-O bonds. Higher temperature H_2S passivation leads to a reduction of the amount of Sulphur at the surface.

We also observe that the presence/absence of S at the interface, as well as the presence of the Al_2O_3 buffer, which has a major impact on the relative peak position in the spectra between the substrate and the overlayer. This will be compared with the electrical characteristics of the stacks.

Finally, we show that using the Sessa software, full quantification of the stack can be obtained under the condition that all instrumental parameters are correctly taken into account.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuA
Probing Spin-Dependent Phenomena

Moderators: Phillip First, Georgia Institute of Technology, Shivani Rajput, Oak Ridge National Laboratory

2:20pm **SP+AS+MI+NS+SS-TuA1 Spin Sensing and Magnetic Design at the Single Atom Level***, **Alexander Khajetoorians**,* Radboud University, The Netherlands **INVITED**

Unraveling many of the current dilemmas in nanoscience hinges on the advancement of techniques which can probe the spin degrees of freedom with high spatial, energy, and ultimately high temporal resolution. With the development of sub-Kelvin high-magnetic field STM, two complementary methods, namely spin-polarized scanning tunneling spectroscopy (SP-STS) [1] and inelastic STS (ISTS) [2-3], can address single spins at the atomic scale with unprecedented precession. While SP-STS reads out the projection of the impurity magnetization, ISTS detects the excitations of this magnetization as a function of an external magnetic field. They are thus the analogs of magnetometry and spin resonance measurements pushed to the single atom limit. We have recently demonstrated that it is possible to reliably combine single atom magnetometry with an atom-by-atom bottom-up fabrication to realize complex atomic-scale magnets with tailored properties [4-6] on metallic surfaces [1,7]. I will discuss the current state of the art of this growing field as it pertains to single spin information storage, and how the functionality of coupled magnetic adatoms can be tailored on surfaces by substrate mediated interactions. I will discuss our recent efforts toward realizing tailored chiral magnets [8] and present an outlook on future perspectives toward probing quantum matter at ultra-low temperatures.

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3:00pm **SP+AS+MI+NS+SS-TuA3 Electron Spin Resonance of Single Atom and Engineered Spin Structures***, **Taeyoung Choi**, W. Paul, C.P. Lutz, A.J. Heinrich,* IBM Almaden Research Center **INVITED**

The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Inelastic spin excitation and spin-polarized tunneling have been employed to study spin physics of individual atoms and engineered structures, demonstrating nanoscale memory bits [1] and logic gates [2]. However, the energy resolution of the STM is mainly limited by a temperature of a system surrounding the atomic spins (>100 µeV).

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [3]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10µeV) while the ESR linewidth is in the range of only a few MHz (~10neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.024\pm0.026}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision [4].

Coherent quantum control of individual atoms on surfaces combined with atom manipulation may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

We gratefully acknowledge financial support from the IBM and Office of Naval Research.

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4:40pm **SP+AS+MI+NS+SS-TuA8 Controlling Kondo Effect of Magnetic Molecules on Au(111) by Small Molecule Binding***, **MinHui Chang**, S.J. Kahng,* Korea University, Republic of Korea*; Y.H. Chang,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H.W. Kim, S.H. Lee,* Korea University, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. Here, we demonstrate that spin interactions of Co-porphyrin on Au(111) can be controlled by adsorption and desorption of small molecules, and be sensed using scanning tunneling microscopy and spectroscopy (STM and STS). Bare Co-porphyrin showed a clear zero-bias peak, a signature of Kondo effect in STS, whereas Co-porphyrin adsorbed small molecules showed modified zero-bias peaks, with reduced full width half maximum or Kondo temperature. Our density functional theory calculation results explain it with spatial redistribution of unpaired spins in d_z2 Orbitals. Our study opens up ways to tune molecular spin interactions by means of chemical binding.

5:00pm **SP+AS+MI+NS+SS-TuA9 Spin-polarized Scanning Tunneling Microscopy on Surfaces Prepared by Molecular Beam Epitaxy***, **Arthur Smith**,* Ohio University Nanoscale and Quantum Phenomena Institute **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) has proven to be a powerful *in-situ* technique for obtaining detailed information about spin structures at surfaces down to atomic scale.[1] It has been applied extensively to investigate pristine ferromagnetic and antiferromagnetic (aFM) transition metal surfaces, with many great results in the case of model systems such as nano-sized magnetic islands and single magnetic monolayers.[2] This has led to fascinating discoveries of nanoscale magnetic domains, domain walls, spin spirals, spin skyrmions, and much more.[3,4] Although not simple in practice, SP-STM can in principle also yield unprecedented spin characterization on a broad spectrum of material surfaces, including practical, real world systems. For example, it could be applied to investigate surfaces of intermetallic compounds, superconductors, complex magnetic oxides, and magnetic semiconductors.

We are applying SP-STM to study various magnetic systems grown *in-situ* by molecular beam epitaxy, including transition metal nitrides,[5] magnetic-doped nitride semiconductors, and several bi-metallic magnetic systems. I will present our recent work using STM and SP-STM, beginning with a discussion of manganese nitrides, including our work on aFM θ-phase MnN and ferrimagnetic ε-phase Mn_4N. The θ-phase films are very complex due to the expectation of canted spins within each atomic layer with four unique canting angles, while the ε-phase films contain two types of spins (Mn^I and Mn^{II}) with equally complex spin arrangements.

A second material we are working on is the chromium nitride system in which we investigate its electronic and spin properties in a low-temperature SP-STM system. Spectroscopy results to date suggest a *d*-wave resonance on the surface and a Kondo signature for nanoscale iron islands grown on atomically-smooth CrN surfaces.

I will also present results for Mn δ-doped semiconducting gallium nitride surfaces in which we find atomic layer ferromagnetism within a unique and stable $\sqrt{3} \times \sqrt{3}$ - R30° MnGaN surface reconstruction. Spectroscopy clearly reveals spin-polarized and spin-split Mn states, as predicted by first principles theory calculations. SP-STM measurements map out ferromagnetic domains at *room temperature*, and the additional presence of magnetic rim states seen at the edges of ferromagnetic islands, as well as magnetic hysteresis, give further interest to this intriguing system.

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[4] S. Loth et al. Science **335**, 196 (2012).

[5] K.K. Wang and A.R. Smith, Nano Lett. **12**, 5443 (2012).

5:40pm **SP+AS+MI+NS+SS-TuA11 The Use of Scanning Probe Techniques to Study the Behaviour of Second Phase Particles in Beryllium and Their Role in Localised Corrosion***, **Christopher Mallinson**, J.F. Watts,* University of Surrey, UK

Scanning Kelvin probe force microscopy (SKPFM) has been employed to examine the galvanic activity of a wide range of second phase particles in S-65 beryllium that are believed to have a role in the localised corrosion of the metal. SKPFM and AFM analysis has been combined with additional surface and bulk analysis techniques of scanning electron microscopy, energy dispersive x-ray spectroscopy and Auger electron spectroscopy to provide a detailed overview of the link between the bulk and surface composition of particles and their Volta potential or surface contact potential.

Initial results appear to show that all second phase particles are more noble than the beryllium matrix with the greatest potential difference observed for $AlFeBe_4$ and alumina or carbide like particles. The more negative Volta potential indicates that the particles should act as local cathodes when the metal is exposed to an aqueous environment.

The initial investigation, which is being performed in-air, will be expanded to determine the effect of increasingly higher humidity environments on the behaviour of the particles. It is hoped that this will provide a greater understanding about the onset of pitting corrosion in beryllium.

6:00pm **SP+AS+MI+NS+SS-TuA12 Many-body Interaction induced Spin-split States of Single Vacancy in Graphite***, **Wonhee Ko**,* Samsung Advanced Institute of Technology, Republic of Korea*; H.W. Kim, Y. Cho,* Samsung Advanced Institute of Technology*; Y. Kuk,* Seoul National University, Korea, Republic of Korea*; S.W. Hwang,* Samsung Advanced Institute of Technology

Although carbon atoms have no magnetic states, it has been known that defects in graphene or graphite can have magnetic states induced by many-body interaction. By utilizing ultra-low-temperature scanning tunneling microscopy, we observed the spin-split states of single vacancy in graphite, which is a hallmark of magnetic states. Evolution of the spin splitting in the magnetic field did not follow the Zeeman effect of single electron states, and can be explained only when we consider electron-electron interaction. Quantitative analysis showed that the strength of the electron-electron interaction is in the range of 1~3 meV. Our observation implies that the simplest defect in graphite like single vacancy can behave as magnetic, which would be an important ingredient for development of carbon-based spintronic devices.

Surface Science
Room 104E - Session SS+AS-TuA
Structure and Characterization of Oxides

Moderator: Robert Bartynski, Rutgers, the State University of New Jersey

2:20pm **SS+AS-TuA1 Phase Formation and Stability of Reactive Sputtered Zirconium Dioxide Thin Films**, ***Mohsin Raza**, D. Cornil, J. Cornil,* University of Mons, Belgium*; S. Lucas,* University of Namur, Belgium*; A.L. Thomann, A. Caillard, M. El Mokh,* GREMI CNRS/Université d'Orléans, France*; J.F. Pierson, P. Boulet,* Université de Lorraine, France*; R. Snyders, S. Konstantinidis,* University of Mons, Belgium

As materials properties are greatly influenced by their phase constitution, therefore it's of high importance to understand and address the mechanisms driving their phase formation and stability. In this respect, zirconium oxide (ZrO$_2$) has been the focus of a special attention for the last couple of decades regarding the stabilization of its cubic (c) phase at room temperature.

In the present study, the role of the film chemistry i.e. of oxygen vacancies and of energy deposited during the film growth is investigated. To this purpose, 100 nm thick films of zirconium oxide are grown in the poisoned mode as well as in the transition zone with the help of voltage feedback control unit (Speedflo mini from Gencoa UK). During the film growth, to have a fast response from the feedback unit and thus a tight control over the film chemistry (i.e. O/Zr ratio), oxygen is injected just at the target surface. By systematically varying the working parameters, it is observed that for films grown at 200 mA, 10 mTorr in the poisoned mode, the XRD diffractograms only exhibits reflections from the low-temperature stable monoclinic (m) phase. To the contrary, while working inside the transition zone i.e. by growing sub-stoichiometric zirconium oxide thin films as demonstrated by careful elemental characterization, the film phase is dramatically modified and only the c reflections are observed. Theoretical calculations at the Density Functional Theory level are in remarkable agreement with the experimental data, hence highlighting that the incorporation of oxygen vacancies is the sole responsible mechanism for the stabilization of the c-phase. It is also observed that any deviation from the optimized working conditions i.e. change in discharge current or pressure leads to the change in film phase constitution. Thermal annealing analysis performed in air and N$_2$ shows the oxygen vacancy stabilized zirconia films are stable up-to 750 °C. Above 750 °C, the mechanical stress, generated in the film due to the mismatch of the thermal expansion coefficients of both the zirconia film and the substrate, apparently surpasses a critical value and leads to the appearance of m-phase.

In conclusion, c-phase of zirconia can be stabilized at room temperature (up to 750 °C) by solely incorporating oxygen vacancies in the zirconia lattice. However, increasing the energy flux during film growth or the mechanical stress may induce the transformation of the oxygen vacancy stabilized cubic phase of zirconia into the m-phase.

2:40pm **SS+AS-TuA2 W-oxide on Ag(100): a Flexible Decoupled 2-D Oxide Layer**, *T. Obermüller, S. Surnev,* ***Falko P. Netzer**,* Karl-Franzens University, Austria

Two-dimensional (2-D) transition metal oxide layers have attracted significant interest during the past decade due to their novel emergent properties and high potential for nanotechnology applications [1,2]. For practical reasons 2-D oxide layers are usually supported on metal surfaces. This leads to a coupling of the oxide overlayer to the metal substrate, thus creating a hybrid system with properties largely determined by the oxide-metal interface. Here, we report the formation of a 2-D W-oxide layer on a Ag(100) surface, where the oxide appears to be essentially *decoupled* from the substrate. The W-oxide has been prepared by vapor phase deposition of (WO$_3$)$_3$ clusters at 500°C substrate temperature. The WO$_x$ grows as a well-ordered incommensurate 2-D wetting layer in large domains with variable orientation with respect to the substrate. This gives rise to a variety of oxide domains with different azimuthal orientation, which can easily be recognized in the STM by their different Moiré patterns. The overlayer lattice can be imaged with atomic resolution in the STM and analyzed using the Moiré formula, from which the square overlayer lattice constant can be accurately evaluated to a = 3.72 Å; this is close to the respective WO$_3$ bulk lattice constant. AES and XPS spectra indicate an overlayer stoichiometry close to WO$_3$, but the W 4f binding energy suggests a lower oxidation state than W^{6+}. A structure model in terms of a 2-D WO$_x$ sheet is discussed. It is conjectured that this WO$_x$ sheet on Ag(100) behaves essentially like an isolated 2-D oxide layer.

[1] G. Pacchioni, *Two-dimensional oxides: multifunctional materials for advanced technologies.* Chem. Eur. J. 18(2012) 10144

[2] *Oxide materials at the two-dimensional limit.* F.P. Netzer, A. Fortunelli, Eds. (Springer Series in Materials Science, April 2016)

3:00pm **SS+AS-TuA3 Growth and Termination of a Rutile IrO2(100) Layer on Ir(111)**, ***Rahul Rai**, T. Li, Z. Liang,* University of Florida, Gainesville*; M. Kim, A. Asthagiri,* Ohio State University*; J.F. Weaver,* University of Florida, Gainesville

Iridium oxide is an effective catalyst for promoting electrochemical water splitting and is a promising material for effecting other chemical transformations as well. In this talk, I will discuss our recent investigations of the growth and termination of a crystalline IrO$_2$(100) film that develops during the oxidation of Ir(111) by gaseous O-atoms. We characterized the oxidation of Ir(111) using temperature programmed desorption (TPD), low energy electron diffraction (LEED), low energy ion scattering spectroscopy (LEISS) and density functional theory (DFT) calculations. We find that a well-ordered surface oxide with ($\sqrt{3} \times \sqrt{3}$)R30° periodicity relative to Ir(111) develops as the oxygen coverage increases to 1.4 ML (monolayer). Continued oxidation produces a rutile IrO$_2$(100) layer that reaches a kinetic saturation, under the conditions employed, after the growth of about four atomic layers and decomposes during TPD to yield a sharp O$_2$ desorption peak at ~770 K. We assert that favorable lattice matching at the IrO$_2$(100)/Ir(111) interface is responsible for the preferential growth of the IrO$_2$(100) facet during the initial oxidation of Ir(111), as LEED reveals the formation of a well-defined (6 × 1) coincidence structure. TPD experiments show that CO and H$_2$O probe molecules bind weakly on the IrO$_2$(100) surface, and LEISS measurements reveal that the oxide surface is strongly enriched in O-atoms. These characteristics provide evidence that the rutile IrO$_2$(100) layer is oxygen-terminated, and therefore lacks reactive Ir atoms that can strongly bind molecular adsorbates. Finally, I will discuss our DFT predictions of the stability of so-called on-top and bridging oxygen atoms on rutile IrO$_2$ and RuO$_2$ surfaces. The DFT results support the conclusion that IrO$_2$(100) is oxygen-terminated at the growth temperatures that we employed (< 650 K), and further reveal that on-top oxygen atoms significantly destabilize bridging oxygen atoms on the rutile (100) surfaces; such destabilization is less pronounced on the (110) surfaces. This destabilization may explain our observation that the desorption of on-top oxygen atoms and complete decomposition of the IrO$_2$(100) film occur over a similar range of temperatures during TPD. Our findings have implications for understanding the generation of rutile IrO$_2$ layers for model surface chemistry studies.

3:20pm **SS+AS-TuA4 Vibrational Spectroscopy of Iron Oxide Nanostructures and Thin Films Supported on Graphite**, ***Joel Langford**, F. Rosner, J.Y. Kwon, J.C. Hemminger,* University of California Irvine

Iron oxide nanostructures supported on highly oriented pyrolytic graphite have been investigated with high resolution electron energy loss spectroscopy (HREELS) and Auger electron spectroscopy (AES). The average O:Fe ratio, as measured by AES, can be increased or decreased by annealing in an oxygen background of 1x10^{-7} Torr or *in vacuo*, respectively. Depending on annealing temperature, and oxygen exposure, the O:Fe ratio can range from near metallic to hematite (Fe$_2$O$_3$) stoichiometry. Regardless of stoichiometry, no iron oxide vibrational modes were observed in the specular HREELS spectra. Only the collective free charge carrier excitation of the graphite substrate was observed. The absence of iron oxide modes in specular HREELS is due to an electrostatic screening from the surface dipole generated by the collective graphite excitation. This screening effect is supported by calculations of the electron energy loss function for a thin iron oxide film supported on graphite. Off specular HREELS shows that the graphite phonon dispersion is unperturbed by the presence of iron oxide nanostructures. Thus, there is minimal interaction between the graphite substrate and the supported iron oxide nanostructures. HREELS spectra of water and carbon monoxide adsorbed on iron oxide nanostructures show hindered vibrational modes. The intensity of the hindered mode is high when compared to the intramolecular modes and the elastic peak. The intensity enhancement is due to a resonance effect between the hindered mode and a longitudinal phonon mode of the nanoparticle i.e. a substrate Fermi resonance. A more descriptive interpretation of this resonant enhancement and finite relaxation lifetime based off perturbation theory will be discussed.

4:20pm **SS+AS-TuA7 Electron Transfer Processes on Single Crsystalline Alkaline Earth Metal Oxide Films*, Thomas Risse,*** Freie Universität Berlin, Germany **INVITED**

Charge transfer processes are central ingredients to understand the chemical and physical properties of matter in general and on surfaces in particular. These processes may be classified into transient charge transfer states as created e.g. after photo excitation and processes, which create metastable charge transfer products such as molecular radicals. The Presentation will be restrict to the discussion of spontaneous charge transfer processes and will among other techniques discuss results obtained by electron paramagnetic resonance (EPR) spectroscopy to characterize paramagnetic species.

We will focus on results obtained on single crystalline, epitaxial MgO(001) film and show how film thickness, defects as well as dopants in the film are involved in charge transfer processes both between intrinsic species within the MgO as well as adsorbates such as molecular oxygen or metal atoms.

5:00pm **SS+AS-TuA9 Tungsten Trioxide Monolayer on Pd(100)***, N. Doudin, M. Blatnik,* Karl-Franzens University, Austria*; D. Kuhness,* Karl-Franzens University, Germany*; A. Fortunelli,* CNR-ICCOM & IPCF Pisa, Italy*; F.P. Netzer,* ***Svetlozar Surnev,*** Karl-Franzens University, Austria

Tungsten trioxide (WO_3) is a key material in several applications including smart windows technology, photo-electrochemical water splitting, gas sensors and heterogeneous catalysis. In particular, tungsten oxides are important acid-base and redox catalysts, and they show excellent activity for many catalytic reactions, such as alcohol dehydrogenation, alkane hydrogenation and metathesis [1]. WO_3 has been produced in single crystal form or as supported thin films with the bulk crystal structure. Recently, the formation of an ordered two-dimensional (2D) tungsten oxide layer on Pt(111) has been reported, where W atoms show a mixture of 5+ and 6+ oxidation states [2].

Here we report on the preparation of a well-ordered 2D WO_3 layer on a Pd(100) surface and the characterization of its geometric, electronic and vibrational structure by a combination of STM, LEED, XPS, HREELS measurements, supported by DFT calculations. The WO_3 monolayer on Pd(100) surface and features a surface network consisting of small (~ 4 nm) square-shaped domains, separated by narrow (~ 0.3 nm) trenches (Fig. 1a). The latter are identified as anti-phase domain boundaries, as evidenced by atomically-resolved STM images (see inset of Fig. 1a) and the characteristic spot splitting in the LEED pattern (Fig. 1b). The STM image shows that each domain exhibits a square surface structure with a lattice constant of 0.39 nm, which corresponds to a c(2x2) superstructure. Another important feature is the presence of few dark depressions inside the domains, which we attribute to missing terminal O atoms (see model in Fig. 1d), in corroboration with HREELS results and high-resolution W 4f core-level spectra (Fig. 1c). The latter consist of three $4f_{7/2}$ - $4f_{5/2}$ doublet components, due to W atoms at different surface locations: within the defect-free areas (major component at 34.4 eV), with missing terminal oxygens (minor component at 33.3 eV), and at the domain boundaries (35.2 eV). The DFT derived structure model of the WO_3 monolayer is shown in Fig. 1d and consists of a layer of O atoms adsorbed in on-top Pd positions, followed by a c(2x2) layer of W atoms, which are connected at the top to terminal O atoms via strong W=O bonds, as suggested by the HREELS results. It can be viewed in a way as a 2D analogue of a cubic $WO_3(001)$ crystal, featuring a similar lattice constant (0.39 nm vs. 0.38 nm) and polyhedral linkage, but with a modified W-O coordination sphere due to the contact with the Pd(100) surface.

[1] D. Gazzoli et al, J. Phys. Chem. B 101 (1997) 11129

[2] Z. Li, et al, J. Phys. Chem. C 115 (2011) 5773

This work has been supported by the FWF Project P26633-N20 and by the EU COST Action CM1104.

5:20pm **SS+AS-TuA10 Electron Energy Loss Study of Excess Electrons in Reducible TiO_2: Dual Behaviour or Coexistence of Trapped and Free States? Bulk or Surface Defects?*, Remi Lazzari,*** *J. Li, J. Jupille,* Institut des NanoSciences de Paris, France

Stoichiometry defects play a tremendous role in the surface chemistry of titanium oxide [1,2]. Reduced rutile is indubitably a n-type semiconductor in terms of electrical transport but electron-based spectroscopies and scanning tunnelling microscopy show the existence of a defect-related gap state lying 0.8-1eV below the Fermi level [1,2]. Its nature *i.e.* surface oxygen vacancies [2,3] versus sub-surface interstitial titaniums [4] is still highly debated in the literature as well the actual (de)localisation of the associated excess electrons [4,5,6].

In our work, electron energy loss spectroscopy in low and high resolution modes was used to probe band gap state and phonon excitations in $TiO_2(110)$ as a function of oxygen exposure at 100 and 300K. By comparing surfaces, from reduced to fully oxidized obtained by various means including electron bombardment, and by using EELS depth sensitivity in out-of-specular detection, a contribution from sub-surface defects is clearly evidenced. A method to prepare defect-free surfaces (as observed by EELS) is even proposed. Using dielectric modelling of spectra including phonons, carriers, gap state and interband transitions and multiple excitations, it was shown that “free-like” carriers characterized by their plasmon excitation coexists with band gap states. While the latter give rise to an obvious peak in the band gap, the former induce a temperature dependent broadening of the quasi-elastic peak and a sizeable screening and upward frequency shift of phonons compared to stoichiometric samples. Through data fitting, both surface and bulk carrier densities and dampings could be quantified as well their profile. A very different dynamics of the healing of the associated signals upon O_2 exposure was also observed. The implication of such findings in terms polaronic nature of excess electron will be discussed.

[1] U. Diebold, Surf. Sci. Rep. 48 (2003) 43; C. Pang *et al.*, Chem. Rev. 113 (2013) 3887

[2] C. Yim *et al.*, Phys. Rev. Lett. 104 (2010) 036806

[3] P. Kruger *et al.*, Phys. Rev. Lett 100 (2008) 055501

[4] S Wendt *et al.*, Science 320 (2008) 1755

[5] M. Setvin *et al.*, Phys. Rev. Lett. 113 (2014) 086402

[6] A. Janotti *et al.*, Phys. Stat. Solidi RRL 7 (2013) 199

6:00pm **SS+AS-TuA12 Vanadium on Anatase TiO_2*, Stig Koust,*** *L. Arnarson,* iNANO, Aarhus University, Denmark*; P.G. Moses,* Haldor Topsøe Research Lab, Denmark*; I. Beinik, J.V. Lauritsen, S. Wendt,* iNANO, Aarhus University, Denmark

Tighter regulations concerning nitrogen oxides (NOx) and an increased public concern, highlighted recently by a study from ICCT [1], demonstrating that new diesel cars emit more than seven times the allowed NOx, has clearly shown the urgent need for the development of more effective catalysts for the removal of NOx. The Selective Catalytic Reduction (SCR) is widely used to reduce NOx into N_2 and H_2O in flue and exhaust gasses. This reaction is best catalyzed using a TiO_2-anatase supported sub-monolayer VOx-based catalyst.

Unfortunately, the detailed reaction mechanism(s) are still debated, and the nature of the active site is uncertain [2]. To tackle these issues, the preparation and characterization of good model catalyst model systems may provide new fundamental insights.

Here we present atomically resolved STM images of sub-monolayer vanadium (V) supported on anatase TiO_2 (101). Upon V deposition at liquid nitrogen temperature (LT), the surface is covered with small isolated V clusters, distributed homogeneously on the terraces. Further characterization with XPS revealed the oxidation state of V being 2+, indicating a preferred binding between V clusters and surface oxygen atoms. This conclusion is further supported by the observed reduction of the titanium surface atoms.

Surprisingly, our STM studies revealed an embedding of vanadium into the near-surface region already at room temperature (RT). A significant decrease in the density of V clusters is observed after annealing at RT and new features in the STM images appeared, which we assign to monomeric V atoms at regular titanium lattice sites, substituting the surface titanium. This change in the surface is accompanied by a shift of the V2p XPS feature to higher binding energy, revealing the oxidation of the vanadium to be 3+/4+ as compared to only 2+ upon LT deposition. The V2p area is unaltered after annealing at RT, suggesting no loss of V due to re-evaporation or migration into the bulk. Our DFT calculations confirm the substitution of vanadium with surface titanium atoms.

Additionally we present STM and XPS studies of vanadia (V_2O_5) depositedon a-TiO_2 (101) in comparison to metallic vanadium on the same surface. Vanadia displays weaker interaction with the surface compared to vanadium and we observe diffusion in to the sub-surface for vanadia after annealing at ~700K, however subsequent oxidation pulls vanadia back out to the surface.

1. Vicente, B., et al. *REAL-WORLD EXHAUST EMISSIONS FROM MODERN DIESEL CARS* . 2014.

2. Busca, G., et al., Applied Catalysis B: Environmental, 1998. (1–2): p. 1-36.

Applied Surface Science
Room Hall D - Session AS-TuP
Applied Surface Science Division Poster Session

AS-TuP2 Observing the Effects of Jetting from Sputtering with Both Monatomic Argon and Argon Gas Clusters of Multi-layered Samples Using XPS with Rapid Mapping*, **Timothy Nunney**,* Thermo Fisher Scientific, UK*; R. Simpson,* University of Surrey, UK*; C. Deeks, P. Mack, J.P.W. Treacy,* Thermo Fisher Scientific, UK

Nano-scale multi-layered materials are becoming more common, especially in the microelectronics industry. Components used in applications such as flexible electrical circuitry are often made of stacked layers of material. These can include both organic and inorganic materials in a single component. Complications arise in depth profiling these kinds of components when transitioning across the interface between the two material types.

Depth profiling from an inorganic layer to an organic layer can produce an effect known as "jetting". This is where material from the lower organic layer is rapidly ejected and redeposited around the etch crater, as a result of the high energy penetration of the inorganic material layer. As soon as the organic layer is exposed to the ion beam, the relative high energy ion beam needed to etch the inorganic layer, will cause material from the organic layer to burst out in this jetting effect.

This presentation will demonstrate the effects of jetting on a range of samples, illustrating how the ejection on deposition occurs depending on the type of sample and the ion beam mode type used. It will show differences between monatomic sputtering and cluster sputtering and showcase the benefits of both of these methods of depth profiling. A new form of rapid XPS mapping will be demonstrated allowing the jetting effect to be quickly observed.

AS-TuP3 Multitechnique Surface Analysis for Advanced Microelectronics Materials*, **James Lallo**,* Thermo Fisher Scientific*; C. Deeks, P. Mack, T.S. Nunney, J.P.W. Treacy,* Thermo Fisher Scientific, UK

Multitechnique analysis is becoming increasingly common for characterisation of materials. Performing X-ray Photoelectron Spectroscopy (XPS) is now routine in many laboratories to give surface information (0-10 nm). Energy Dispersive X-ray Spectroscopy (EDS or EDX) is also widely used in laboratories to help detect elemental information from smaller areas within the bulk (1-2 µm) of the material. A combination of both EDS and XPS can help to give a wider picture of samples being analysed, giving both elemental and chemical information from both the 'surface' and the 'bulk' of samples over a wide ranging spatial area.

EDS is often used in microelectronics laboratories to observe if any contaminants are present on the surface. A big contaminant is copper as it has poor adhesion to most insulators, so the ability to observe this is key. We will demonstrate on advanced microelectronic samples that EDS alone is not enough for detecting contaminants such as this, and we will show that XPS is also needed to give the full elemental and chemical details of these types of samples.

This presentation will look at a range of microelectronics samples, and demonstrate by using both XPS and EDS combined on a single system, that no one technique is enough to obtain the full picture of what is in the sample, and show that by having the ability to have both these techniques on a single system, it can provide a wealth of complementary information from the surface and near-surface regions of a material.

AS-TuP4 Surface Analysis of Human Hair – a Multi-technique Approach*, **Sarah Coultas**, J.D.P. Counsell, C.J. Blomfield,* Kratos Analytical Limited, UK*; M. Openshaw,* Shimadzu - MALDI Technologies Group*; C. Moffitt,* Kratos Analytical Inc.

In 2016, the global hair care market is estimated to be worth about USD 83.1 billion [1] and the size of the market is growing year on year. There are thousands of products available used for both cosmetic and medical purposes and the industry is constantly developing new formulations to improve performance and safety.

There are numerous treatments and modifications made to hair which involve complex surface chemistry. Products contain many ingredients designed to clean, condition, add volume, shine or treat medical conditions such as dandruff to name but a few. Techniques such as XPS, ToF-SIMS and MALDI-ToF have all been used to characterise the surfaces of natural fibres and investigate the efficacy of such treatments. Recent developments in organic depth profiling using argon cluster sources have also been applied to hair samples opening up an interesting extra dimension [2].

Each of the techniques has its own strengths: XPS provides quantitative elemental identification whereas ToF-SIMS and MALDI are rich in molecular information. Here we use the combination of all three to fully characterise the surface treatment of human hair, in particular the application of conditioner. A range of treatment conditions have been studied, including various concentrations of active ingredients and application methods. As well as investigating the distribution with depth using ARXPS and cluster depth profiling we explore the spatial distribution of species via imaging.

[1] http://www.statista.com/statistics/254608/global-hair-care-market-size/

[2] Ishikawa, Kazutaka and Okamoto, Masayuki and Aoyagi, Satoka, Biointerphases, 11, 02A315 (2016)

AS-TuP5 Exploring the Surface and Sub-Surface Nature of Nuclear Graphite*, J.D.P. Counsell, S.J. Coultas, C.J. Blomfield,* Kratos Analytical Limited, UK*; **Chris Moffitt**,* Kratos Analytical Limited*; A. Theodosiou,* University of Manchester

Graphite is a key material used in the current generation of UK nuclear reactors. Graphite has been recognised as an excellent neutron moderator and reflector in reactors, allowing sustainable, controlled fission. Contaminants in moderator rods are a major problem as they can act as neutron absorbers. This causes decreased fission and production of unwanted isotopes – a common cause of radioactive waste. The goal of this study is to understand the surface chemistry of graphites used in the UK nuclear industry today.

The surface compositions of Pile grade A (PGA) and Gliso coke graphites are determined using X-ray photoelectron spectroscopy (XPS). The results are compared to commercially available highly-ordered pyrolytic graphite (HOPG). The degree of sp2/sp3 character is determined for each graphite using Auger parameter analysis. Significant variation in sp2 character was observed between graphites. Depth profiling of the surface was performed utilising both monatomic Ar+ ions and cluster Arn+ ions. The mechanics of cluster/monatomic ion bombardment are discussed with respect to surface damage and a suitable method for graphite bulk analysis is proposed.

AS-TuP6 Comparison of Angle Resolved XPS and Ultra-shallow Ar Gas Cluster Depth Profiling of Organometallic Multilayer Materials*, **Simon Hutton**,* Kratos Analytical Limited, UK*; T. Bendikov,* Weizmann Institute of Science, Israel*; K. Macak, W. Boxford, S.C. Page, S.J. Coultas, C.J. Blomfield, J.D.P. Counsell,* Kratos Analytical Limited, UK

Angle resolved X-ray photoelectron spectroscopy (ARXPS) is a widely used technique for investigating the depth distribution of species over the first few nanometres of the sample surface. An important property of the technique is that it is non-destructive; the sample is not damaged during the measurement process. This is in contrast to sputter depth profiling where an ion beam removes the surface layer to reveal the underlying material. A major shortcoming of the ARXPS technique is that it provides information only from the surface region of the material. It is limited to the maximum escape depth of the photoelectrons generated during measurement. This limitation is not shared by sputter depth profiling, which can delve deep into the material by employing multiple sputter / analysis cycles.

Chemical damage of the analysed material is an ever present consideration during sputter profiling. One method of reducing this chemical damage is to vary the nature of the sputtering ion. This has proved very successful for organic materials and thin films where massive gas cluster ions have found widespread use. We have previously demonstrated the successful use of massive Ar clusters to sputter depth profile through multi-layer organometallic thin films [1]. In this study we compare the results of non-destructive ARXPS measurements with ultra-shallow sputter depth profiling using massive Ar cluster ions on similar multi-layer organometallic thin films.

The films consist of two well defined and iso-structural osmium and ruthenium polypridyl complexes. These complexes are deposited from solution in a sequence-dependent assembly regime leading to self-propagating molecular assemblies with distinct internal interfaces and composition. [2] The films were assembled on indium tin oxide (ITO) coated glass slides. ARXPS data was collected by tilting the sample with respect to the analyser / X-ray source. The results were processed using a maximum entropy method software package developed specifically for this type of application [3].

Shallow sputter profiles through the thin films were achieved using massive Ar cluster ions with approximately 2000 Ar atoms per cluster. Ion acceleration voltages were kept low to ensure a very low energy per Ar atom and hence limit the sputtered region to the sample surface.

[1] S. Hutton, T. Bendikov, W. Boxford, S. Page, J. Counsell, A. Roberts, C. Blomfield, S. Coultas, *AS-THP3* AVS 62nd International Symposium & Exhibition.

[2] G. de Ruiter, M. Lahav, G. Evmenenko, P. Dutta, D. A. Cristaldi, A. Gulino and M. E. van der Boom, *J. Am. Chem. Soc.* 2013, 135, 16533-16544.

[3] K. Macak*, Surf. Interface. Anal.* 2011.

AS-TuP7 Pd deposited on Al_2O_3 analyzed by Low Energy Ion Scattering (LEIS)*, P. Bruener, T. Grehl,* ION-TOF GmbH, Germany*; **Nathan Havercroft**,* ION-TOF USA*; J.Z. Mundy, G.N. Parsons,* North Carolina State University

Low Energy Ion Scattering (LEIS) is uniquely able to provide quantitative elemental characterization of the outermost atomic layer of a sample. In addition, the LEIS spectra contain information about the composition of the first few nm of the samples. These properties make it an ideal tool for the characterization of thin films, from the initial nucleation stage to complete films. The analysis gives insight into growth modes (island vs. layer-by-layer), growth rates and impurities, as well as accurate information about layer closure.

For the LEIS analysis, noble gas ions with kinetic energy of a few keV are scattered by individual atoms in the sample surface. The energy loss of the ions in this scattering process is dependent on the mass of the surface atom it was scattered from. The peaks in the energy spectrum of the backscattered ions are used to identify and quantify the elemental composition of the outer surface.

Ions that are scattered in deeper atomic layers are first of all efficiently neutralized and lose energy by nuclear and electronic stopping on their way through the sample. This causes a shift in energy proportional to the distance traveled in the solid, and a lower intensity of those ions. Due to this, the scattering from the first atomic layer can be distinguished from sub-surface scattering, leading to the extreme surface sensitivity of just one atomic layer [1].

However, even ions scattered below the surface can be detected if the surface promotes the reionization of neutralized primary ions after their travel through sub-surface layers. This can be used to determine layer thickness and elemental distribution in the first few nm of the sample in a fast and non-destructive measurement. The required stopping power values are calculated using SRIM [2].

In this study we applied LEIS to a range of samples of ALD deposited Pd on Al_2O_3 substrates. The currently used process for the Pd deposition requires high temperatures to facilitate the desorption of residuals from the Pd precursor, which poison the substrate surface and inhibit the further nucleation of Pd. This leads to island growth of Pd clusters. We demonstrate how LEIS can be used to analyze the surface coverage of the deposited Pd, the Pd cluster dimensions, and the amount of precursor residual. This information is crucial to develop a lower temperature process for the deposition on temperature sensitive substrates, such as polymers.

[1] Surface composition analysis by low-energy ion scattering, Brongersma, H. H.; Draxler et al., Surf Sci Reports, 62, 2007, 63-109

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AS-TuP8 Real-time Monitoring of Surface Reactions by Means of Cluster-induced Desorption/Ionization Mass Spectrometry*, A. Portz,* Justus Liebig University Giessen, Germany*; **ChristophR. Gebhardt**,* Bruker Daltonics Bremen, Germany*; M. Durr,* Justus Liebig University Giessen, Germany

The reactions of biomolecules on surfaces are of great interest both from a fundamental point of view as well as with respect to applications such as surface functionalization. However, the chemical information obtained by standard surface analysis tools is limited. Recently, we have shown that desorption/ionization induced by neutral clusters (DINeC) is a soft and matrix-free ion source for mass spectrometry of biomolecules. DINeC employs molecular clusters of 10^3 to 10^4 SO_2 molecules; the clusters do not only provide the energy necessary for desorption but, due to the high dipole moment of SO_2, also serve as a transient matrix in which the desorbing molecule is dissolved during cluster-surface impact. Thus desorption takes place at comparably low cluster energies (< 1eV/molecule); shattering of the clusters during and after surface impact furthermore leads to a rapid redistribution of the system's energy. As a consequence, desorption takes place without fragmentation of the desorbing molecules.

In this contribution, we demonstrate that DINeC can be used for real-time monitoring of surface reactions of larger molecules such as porphyrins and oligo-peptides. The quantitative nature of the method was demonstrated using angiotensin II molecules individually adsorbed on gold substrates by means of electrospray ion-beam deposition. These adsorbates were desorbed and detected as intact molecules down to a coverage of 10^{-13} mol/cm^2 (0.001 ML); a linear relationship between surface coverage and signal intensity was observed over three orders of magnitude. Real-time monitoring of surface reactions is demonstrated for isotope-exchange experiments with angiotensin II and different types of porphyrins. Dosing D_2O led to a broadening of the isotopic pattern and a continuous shift towards higher m/z values. When the D_2O pressure was chosen high enough, the H/D exchange rate was determined by the exchange process itself. The results were modeled by means of Monte Carlo simulations taking into account reaction and back-reaction of H/D exchange. Several different rate constants could be extracted and are assigned to the different types of functional groups in the respective molecules.

AS-TuP9 Improved X-ray Photoelectron Spectroscopy Analysis using the PHI *VersaProbe* III*, **Jennifer Mann**, J.S. Hammond, J.F. Moulder, B. Schmidt,* Physical Electronics USA

Based on its proven scanning X-ray Photoelectron Spectroscopy (XPS) microprobe core technology, Physical Electronics has introduced the newest version of its *VersaProbe* product line; the *VersaProbe* III. Multiple improvements over the *VersaProbe* II model have been incorporated into this new design including:

1. Higher sensitivity for all analysis areas
2. Increased number of detector channels for faster imaging
3. Collection angle defining aperture for angle dependent studies
4. Improved hot/cold stage temperature range
5. Dedicated high temperature mount for increased temperature experiments
6. Dedicated 4-contact sample mount for in-situ controlled potential experiments

This poster will discuss these improvements in more detail and show examples where they are beneficial in XPS experiments.

AS-TuP10 Multiple Technique Investigation of UV-grafted Polymers*, **Lopamudra Das**, M.J. Kelley,* College of William and Mary

The major increased-value opportunities for polyesters depend on affordable, environmentally-friendly surface modification. We report the use of 172 nm UV light to induce surface radicals that offer graft sites for desirable functionalities on PET, PTT, PBT and PEN. Obtaining insight into the mechanisms and results requires multiple techniques, notably XPS, ToF-SIMS, AFM and FTIR.

AS-TuP11 Analysis of Thin Phase-Shifter Films using Surface Analysis Techniques*, **Vincent Smentkowski**,* General Electric Global Research Center*; L. Le Tarte,* GGeneral Electric Global Research Center*; H. Piao,* General Electric Global Research Center*; M. Marko,* Wadsworth Center

Many types of phase-shifters have been developed for use in place of the TEM objective aperture. The phase shifters act to increase phase contrast by providing high transfer of information over a very wide spatial-frequency range. Unfortunately, many of these devices fail shortly after being installed into the instrument due to charging in the electron beam, so we have been experimenting with surface deposition of novel thin-film metals. In some cases, it is essential that the electron-scattering cross-section of the metal film be as small as possible, so the films must often be quite thin (less than 10 nm thick). Accurate analysis of such thin films is required to understand the composition of the layers, unexpected impurities both in the films and at the interfaces, the oxidation state of the layers, and the lateral uniformity of the layers.

In this poster we use a suite of surface analysis techniques to monitor the distribution of species through one multilayer phase plate stack comprised of 2nm Rh, 6nm C, and 2nm Al using depth profiling protocol. The pros and cons of each of the surface analysis techniques are illustrated via the sample analyzed. Each of the three techniques used here were able to successfully identify and resolve each of the 3 layers with a sufficient number of data points defining the thin layers. Each of the techniques also revealed oxygen in the aluminum layer with a stoichiometry of about Al_2O_3.

An advantage of ToF-SIMS for depth profiling is the ability to rapidly collect an image at every depth, allowing for 3D rendering of the data sets. The 3D ToF-SIMS renderings do not reveal discontinuous regions at a length scale of a few hundred nm (the conditions used here); ruling out holes at a length scale of less than a few hundred nanometers in the Rh layer would require ToF-SIMS analysis using a pulsing mode with a smaller analytical spot size. Another advantage of ToF-SIMS is that a full mass spectrum is saved at every voxel and hence all elements and high mass molecular fragments are analyzed. Often unexpected species are revealed sub surface. A disadvantage of ToF-SIMS is the ion yield varies depending on the composition of the matrix and this makes quantitative analysis more difficult. In contrast sensitivity factors have been developed for both AES and XPS and these reported sensitivity factors are typically valid to within 10% and hence quantitative analysis is easier.

Mike Marco acknowledges funding through NIH grant GM103555.

AS-TuP12 Improving the Performance of the Cylindrical Mirror Analyzer by Electrode Segmentation*, David Edwards, Jr,* IJL Research Center

Electrode segmentation of the cylindrical mirror analyzer has been shown to significantly improve the resolution of the standard instrument. The high precision solution which had been found for the 42.3 device is shown in this report to exist in fact for an extended set of input angles or equivalently for a range of sample positions. This has allowed a significant limitation of the CMA, namely the critical dependence of instrument performance on sample position, to be largely overcome. In addition by placing the sample at the minimum in the curve of resolution vs sample position, a resolution of ~.000045 has been obtained for a +-6 degree bundle an improvement of a factor of ~40 over the standard spectrometer. Thus electrode segmentation has been found not only to significantly improve the device performance, but in fact to enable its high precision to be realized.

AS-TuP15 Impact of Surface Contaminants on ToF-SIMS analysis of Wood Polymer Composites (WPCs)*, Laura D. Brunelle*, *Z.A. Gernold, C.S. Swagler, E.R. Welton, R.E. Goacher,* Niagara University

Wood Polymer Composites (WPCs) are a promising material for outdoor applications, such as decking and marine structures, because they have improved properties over wood or plastic alone. WPCs also allow for the recycling of plastics and use of reclaimed wood. However, the use of WPCs poses questions regarding the breakdown and weathering of WPCs. The importance of the interface between wood and polymer components of the composite may make analysis with a chemical imaging technique such as Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) advantageous. Due to the high surface sensitivity of ToF-SIMS, an understanding of the surface contaminants on WPCs is required. Contaminants on WPCs may arise from handling, storage, or from lubricants and other components used in the manufacturing process. As such, even new material surfaces can be considered contaminated. Therefore, the interiors of the WPCs were used as references, as the interior is an unhandled surface. The removal of contaminants by solvents (including purified water, isopropyl alcohol, and mixtures thereof) was evaluated to identify appropriate cleaning methods. Furthermore, it may be desirable to remove contaminants prior to or after controlled weathering experiments. Therefore, the chosen cleaning method was applied to previously weathered samples. Comparisons of ToF-SIMS spectra of the WPCs were performed using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR). This work provides insight into how the surface and interior of the WPCs differ, how treatment with common solvents alter the obtained spectra, and how weathered surfaces appear with and without cleaning.

AS-TuP16 Examining the General Applicability of ToF-SIMS for Wood Polymer Composite (WPC) Analysis*, Christopher S. Swagler*, *L.D. Brunelle, M.R. Michienzi, E.R. Welton, R.E. Goacher,* Niagara University

The interface between hydrophobic plastic and hydrophilic wood in Wood Polymer Composites (WPCs) is important for the strength and durability of the materials. WPCs are used in decking and marine structures because they have improved properties over wood or plastic alone. WPCs are relatively new materials and prior research into their weathering and durability has focused on the issue of interface adhesion. Such studies have used Scanning Electron Microscopy (SEM) for morphological analysis, and many have included chemical analysis using X-ray Photoelectron Spectroscopy (XPS). However, XPS has poor imaging resolution and only provides elemental and functional group analysis. For a more detailed analysis of the wood-plastic interface, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) offers higher imaging resolution than XPS, and can provide more detailed molecular information. To date, ToF-SIMS analysis of WPCs has been limited to preliminary studies involving the weathering and cleaning of a single commercially available product. These analyses have shown ToF-SIMS to have promise for the analysis of weathering, using spectral, imaging, and depth profiling approaches. The present study expands this analysis to include a wider variety of sample types, such as those made from polypropylene, nylon or styrene maleic anhydride plastics, with and without added dyes. The composition of these samples is better known than the composition of the previously analyzed commercial material, which aids in identification of peaks from the polymer, wood, and any additives. The analysis of a wider set of unweathered WPCs provides baseline information about the observable chemical distributions for comparison to weathered samples. ToF-SIMS results are also compared to visual light microscopy, SEM, and XPS to illustrate complementarity with these techniques. This work provides insight into how the ToF-SIMS spectra and images vary for WPCs of different composition, including new and reclaimed materials.

AS-TuP17 Swift Heavy Ion Irradiation for Designing Planar Field Emitters and Exchange Bias Layers*, Debalaya Sarker*[*], *S. Bhattacharya,* Indian Institute of Technology Delhi, India*; S. Ghosh, P. Srivastava,* Indian Institute of Technology Delhi

In this talk, I shall give a brief overview of engineering ferromagnetic metal-insulator (FM_M/SiO_2 FM_M=FeCo, Ni) nano-composites having application in device physics. Increasing demand of flat displays necessitates to design planar emitters which not only miniaturize the device but also have several other advantages like mechanical durability, temporal stability etc. FM_M nanoparticles (NPs) inside SiO_2 matrix, when subjected to Swift Heavy Ion (SHI) irradiations get elongated. Using this, we demonstrate here a planar field emitter with maximum current density of 550 $\mu A/cm^2$ at an applied field of 15 V/μm. The film, irradiated with 5×10^{13} ions/cm^2 fluence (5e13) of 120 MeV Au^{9+} ions, shows very high electron emitting quantum efficiency in comparison to its unirradiated counterpart. We find experimental evidence of enhanced valence band (VB) density of states (DOS) for 5e13 film from XPS, which is further verified in the electronic structure of a model FM_M cluster from combined density functional theory (DFT) and *ab initio* molecular dynamics (MD) simulations. The MD temperature is taken from the lattice temperature profile from thermal spike model. Increasing the SHI fluence beyond 5e13, results in reduced VB DOS and melting of surface protrusions, thus causing reduction of FE current density. We finally conclude from DFT that change in fluence alters the co-ordination chemistry followed by the charge distribution and spin alignment, which influence the VB DOS and concurrent FE as evident from our experiment.[1,2] More recently, we have explored the effect of shape and structural anisotropies on magnetic properties of SHI irradiated FM_M/SiO_2 flims. Magnetic anisotropy (MA) and exchange bias effect (EBE) were tuned by monitoring SHI irradiation fluence. The in-plane and out-of-plane M-H loops show that the perpendicular MA reaches a maximum value at 5e13 and then decreases. At highest fluence an EBE is observed. Underlying electronic structure was not only probed with XANES and XPS VB, but also is validated from our non-collinear theoretical calculations. We conclude this EBE is an outcome of formation of anti-ferromagnetic domains due to spin-flipping at high temperature. In summary, elongated FM_M NPs inside SiO_2 matrix are designed using controlled SHI irradiation. Due to its high current density and mechanical/chemical durability, the irradiated films open new possibilities for the development of electronic displays. They also show sufficient promise in magnetic storage media for their interesting MA and EBE properties.

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AS-TuP18 Improving Relative Quantitation in Imaging Lipidomics using ToF-SIMS*, Marwa Munem*, *J.S. Fletcher,* University of Gothenburg, Sweden

Introduction

ToF-SIMS is of increasing value to clinicians and has been used on a number of tissue samples to successfully identify and localise different chemical components to various areas of the tissue and answer disease related questions [1]. Compared to traditional histology or fluorescence staining, the main advantage of ToF-SIMS is the label free detection of a large number of different molecules simultaneously on the same tissue section. New gas cluster ion beams (GCIBs) provides benefits for imaging larger molecular species [2]. These improvements still leave issues such as greatly varying ionisation efficiencies for different molecules and matrix effects. In

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[*] **National Student Award Finalist**

some biological samples changes in Na or K concentration through the sample can lead to different pseudo-molecular ions being preferentially generated from different parts of the sample.

Methods

A J105 ToF-SIMS instrument (Ionoptika Ltd, UK) was used to analyse salt adduct effects on lipids ionization by exposing different standard lipids and tissue samples to different concentrations of sodium and potassium salts mixtures. Tissue sections from mouse heart, rat brain and cancer biopsy samples were imaged on the same instrument adduct formation assessed.

Results

In positive ion mode the relative intensity of $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$ ions from phospatidylcholine phospholipids changes dramatically with just a small change in in the Na:K ratio in the sample. The situation is further complicated by changes in relative intensities of fragment ions. The ratio of the $[M+Na-59]^+$ to the $[M+Na]^+$ peak is significantly smaller than the equivalent ratio from potassium adduct ions. Using these different peaks corrected images of different lipids can be generated from images of tissue sections obtained by ToF-SIMS.

Conclusions

Matrix effects, in this case variation in salt content in biological samples, can lead to difficulties in (relative) quantitation of different biological species. The changes in ionisation and fragmentation observed in ToF-SIMS measurements show similar trends to those observed with other mass spectrometry methods where adduct formation is used as a tool for influencing fragmentation in tandem MS experiments[3].

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AS-TuP19 XPS Investigation of UHP Mg and Mg Alloys Exposed to Water: Peak Fitting the Mg 2p Core Level Spectra to Distinguish Oxide from Hydroxide, ***Harry Meyer***, *D. Leonard, M.P. Brady,* Oak Ridge National Laboratory

Magnesium alloys are increasingly used in structural materials applications requiring high strength and light weight. Alloys containing Mg are also of interest in biomedical applications (implants) and energy materials applications (fuel cells, batteries, and hydrogen storage). The Department of Energy has aggressive materials research projects aimed at increasing the use of magnesium and magnesium-based alloys for vehicle applications. The primary interest in vehicles is to reduce the overall vehicle weight by substituting lighter weight Mg-alloys. One of the primary obstacles for increased use of Mg-alloys is the corrosion behavior of these materials. Oak Ridge National Laboratory has been studying aqueous corrosion behavior for several years to try to develop an understanding of the carrion film formation mechanism. The material presented in this poster is a portion of that larger program and is focused on using x-ray photoelectron spectroscopy (XPS) to study Mg-alloy corrosion. In this study we have exposed four Mg materials (UHP Mg; Mg-0.27Zr; Mg-0.14Nd; and Mg-2Al) to water for 4 hours to elucidate early film formation. Ar-ion depth profiling was used to compare the thickness of the corrosion films and to try to understand the partitioning between oxide and hydroxide growth. This poster demonstrates the Mg 2p peak fitting strategy that was employed. This abstract has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.

AS-TuP20 Root-Cause Analysis of an Interfacial Adhesive Failure Based on Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), ***James Ohlhausen***, *P. Vianco,* Sandia National Laboratories

Low Temperature Co-fired Ceramic (LTTC) substrates are used for high frequency electronics assemblies. The LTCC material is comprised of alumina particles in a silica-based, glassy phase; the latter also includes Na, Mg and Ca oxides. The surface conductor traces and pads are a Au/Pt/Cu/Ti metallization where Ti is the adhesion layer. Delamination was experienced at the interface between the Ti layer and LTCC. Determining a root-cause to the delamination was made difficult by the complexity of the LTCC material and air exposure of the test samples before being introduced into the vacuum chamber for surface analysis. This air exposure of already de-adhered interfaces potentially compromises the cleanliness of the mutual, interface surfaces due to oxidation and adventitious contamination that caused significant challenge for the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) assessment.

ToF-SIMS was used to analyze the de-adhered interfaces as well as to evaluate the unexposed interface by means of the depth profile mode. The ToF-SIMS tool was able to identify key Pb, Na, K, and Ca markers that confirmed the widespread coverage of the surface by the glassy phase. The role of organic contamination was similarly documented at the de-adhesion sites. The data obtained from these ToF-SIMS assessments confirmed that delamination was caused primarily by the propensity of the glassy phase to cover the LTCC surface. Small variations to the glass phase composition accounted for the intermittent presence of delamination. This poster will outline the specific ToF-SIMS test steps as well as the data analysis and methodologies that allowed for a conclusion to be developed for the delamination event.

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

AS-TuP21 Surface and Bulk Property Studies of Newly Developed High Performance Transparent Conductor Material, ***Lei Zhang***, *W. Wu, N.G. Tassi, D. Walls,* DuPont Science and Engineering

Nowadays, transparent conductor (TC) materials have been widely applied into various areas including displays such as LCD & OLED, touchscreens, and photovoltaics. While indium tin oxide (ITO) has been used as a dominant TC material, due to the rareness of indium metal, scientists have been working to develop new/alternative TC materials to meet special needs in different application areas.

In the area for large touch screen panel application, copper mesh material can be a good TC candidate because of Cu's high electrical conductivity and low material cost. However, Cu is unstable in air and easily forms Cu(I)/Cu(II) oxides, plus Cu atoms are easily diffused to other layers in the devices to cause device malfunctioning. To stabilize the Cu surfaces, graphene is selectively deposited on the surfaces of the micro-grids by atmospheric pressure chemical vapor deposition (CVD) method. Integrated analytical techniques including X-ray photoelectron spectroscopy (XPS), Raman, and others were applied to characterize the surface, bulk, and electrical properties of the graphene coated Cu/Ni micro-grid systems. Results indicated the realization of long-term stability of the new TC structure. This presentation will cover the development and study of this high performance and stable graphene coated copper/nickel micro-grids transparent conducting structure.

AS-TuP22 Optimizing the Surface of Perovskite Oxide/Carbon Composites as Catalysts for the Oxygen Reduction Reaction in Alkaline Media, ***Michael Dzara***, *C. Ngo,* Colorado School of Mines; *J. Christ,* National Renewable Energy Laboratory; *P. Joghee, C. Cadigan, T. Batson, R. Richards, R. O'Hayre, S. Pylypenko,* Colorado School of Mines

Developing non-precious metal catalyst (NPMC) materials for the oxygen reduction reaction (ORR) is a critical research area in order to drive the widespread commercial adoption of low temperature fuel cells. Current technology uses Pt or other precious metal-based catalysts; by replacing these expensive precious metals with inexpensive, earth-abundant NPMCs, the economic feasibility of low temperature fuel cells can be significantly improved. However, improvements in the performance of NPMCs are needed in order to compete with precious metal-based catalysts. Perovskite oxide structures (ABO_3)are one of the candidates among themany materials being evaluated as NPMCs for the ORR in alkaline media. Many elements can form perovskite oxide structures that are stable in alkaline media, and the properties of these structures can be tuned by doping the A and B sites, providing an extremely vast range of possible structures to explore.[1] Performance of perovskite oxides has been shown to improve by creating a perovskite oxide/carbon composite, as carbon improves the conductivity of the composite and has an active role in catalyzing the ORR.[2] However, like other NPMC chemistries perovskite oxides are heterogeneous by nature, and it is therefore difficult to correlate material properties with catalytic performance.

Here, our work focuses on understanding the interplay of surface chemistry and surface morphology of $Ca_{0.9}La_{0.1}Al_{0.1}Mn_{0.9}O_{3-\delta}$ perovskite oxides and their composites with carbon. An aerogel synthesis method was used to produce $Ca_{0.9}La_{0.1}Al_{0.1}Mn_{0.9}O_{3-\delta}$ perovskite oxides with surface areas from approximately 5-80 m^2/g. By varying synthesis parameters, materials with different surface chemistry and morphology were produced. Detailed characterization of surface composition and morphology are performed using physisorption, x-ray photoelectron spectroscopy, and transmission electron microscopy equipped with energy dispersive X-ray spectroscopy. This information is correlated to rotating ring-disk electrode electrochemical measurements in alkaline media. These techniques help provide understanding of the surface properties of $Ca_{0.9}La_{0.1}Al_{0.1}Mn_{0.9}O_{3-\delta}$ perovskite oxides and their impact on performance, providing a path towards optimization of the surface chemistry and morphology for improved catalytic performance.

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AS-TuP23 Tuning of N-Doping in Carbon Nanospheres for Investigation of Catalyst-Support Interactions*, Matthew Strand,* *C. Ngo, A. White, J. Hagen, S. Pylypenko,* Colorado School of Mines

Continued increase of worldwide energy consumption necessitates the development of renewable energy resources. Fuel cells can utilize a wide variety of renewable fuels, but poor long term stability of the catalyst impacts their economic viability. High surface area carbon is utilized as a state-of-the-art catalyst support, and research has shown that the presence of dopants such as nitrogen can improve the stability of catalyst nanoparticles.[1,2] The interplay between nitrogen concentration, graphiticity, and specific nitrogen functionalities and their effect on catalyst-support interactions is still not well understood. Such investigations require the use of model high-surface area materials and multi-technique characterization approach.

In this work, a series of nitrogen-doped carbons was created to serve as model high-surface area substrates with the goal to: investigate in more detail the effect of nitrogen and specific nitrogen functionalities on the stability of metal nanoparticles; enable in situ microscopy analysis of catalyst-support interactions; and serve as a platform for atomistic analysis of dopants in high-surface area carbon materials. N-doped carbon nanospheres were synthesized using a previously published sol-gel method,[3] varying both the amount of nitrogen precursor and pyrolysis temperature in order to vary nitrogen concentration and speciation. Samples were first characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) to determine nanosphere sizes, then by nitrogen physisorption for surface area and porosity analysis. Detailed analysis with Raman and X-ray photoelectron spectroscopies was completed to correlate changes to the parameter space of the synthesis with ratio of amorphous to graphitic carbon, relative concentrations of nitrogen, and different nitrogen functionalities.

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AS-TuP24 Electron Microscopy Study of Fission Product Migration in Irradiated TRISO Nuclear Fuel*, Rachel Seibert,* Illinois Institute of Technology*; C. Parish, P. Edmondson, K. Terrani,* Oak Ridge National Laboratory*; J. Terry,* Illinois Institute of Technology

High temperature gas cooled reactors (HTGRs) may use tristructural-isotropic (TRISO) coated nuclear fuel particles. Fuel performance is limited by the interaction of fission products with the barrier SiC layer. In particular, Ag is released from intact TRISO fuel, and Pd may locally corrode the SiC. Additionally, uranium and plutonium migration are of interest. An understanding of the reaction mechanisms and kinetics of these interactions under normal operation as well as accident conditions is critical for the development of advanced nuclear reactors. We have studied TRISO particles produced at ORNL under the Advanced Gas Reactor fuel program. The fuel was irradiated at the Advanced Test Reactor at Idaho National Laboratory. The local chemical structure of three TRISO SiC shells was examined through X-ray absorption fine structure spectroscopy (XAFS) at the Materials Research Collaborative Access beamline at the Advanced Photon Source. To complement these results, electron microscopy studies have been conducted on various samples prepared from these SiC fragments at the Low Activation Materials Development and Analysis (LAMDA) facility at ORNL. Specifically, samples were prepared from the inner, outer, and middle interfaces of the SiC fragment to obtain a full cross-sectional image of the fission product migration. These results have provided key information on the fission product transport behavior through irradiated SiC at varying temperatures. Knowledge of these reaction pathways will allow for better simulation of the long-term behavior of TRISO fuels. They may also suggest ways to modify the SiC layer to improve fuel performance and mitigate fission product release, which is critical for safety strategies required to commercialize HTGRs.

AS-TuP26 X-ray Photoelectron Spectroscopy Analysis of Titanium Nitride-Nickel Nanocomposite Catalyst*, Samuel Gage,* Colorado School of Mines*; V. Molinari, D. Esposito,* Max Planck Institute of Colloids and Interfaces, Germany*; S. Pylypenko,* Colorado School of Mines

Titanium nitride-nickel (TiN-Ni) nanocomposites have been recently found to be an efficient catalyst for the hydrogenolysis of aryl ethers as models for lignin biomass refining. As compared to Ni catalysts supported on carbon, TiN-Ni nanocomposites showed superior catalytic activity. One possible explanation for the improved performance is a change in the electronic structure of nickel due to the TiN support. In order to test this hypothesis, a series of TiN-Ni nanocomposites with varying amounts of Ni loadings (1, 10, 20 and 50 wt.%) were synthesized and investigated using X-ray Photoelectron spectroscopy (XPS) and microscopy techniques. A series of TiO_2-Ni reference materials with identical Ni loadings served as a reference.

The binding energy of Ni in the TiN-Ni samples is higher than those measured for Ni supported on TiO_2, indicating that Ni in TiN-Ni nanocomposites is more electron poor. At Ni loadings greater than 1 wt.%, higher concentrations of Ni were measured on the surface of the TiN support as compared to the TiO_2 support. The increase in the Ni loading appears to preferentially block TiN surface sites. In contrast at 1 wt.% loadings, the amount of Ni detected on the surface of TiN support is lower than that observed on the surface of TiO_2 support, suggesting incorporation of Ni into the TiN structure.

AS-TuP27 Redox Active Cerium Oxide Immobilized on Highly Ordered Polymer Nanopillars as Dopamine Sensor*, Swetha Barkam*[*]*, M. Peppler, S. Das, S. Saraf, C. Li, J. Thomas, S. Seal,* University of Central Florida

Dopamine, is one of the main neurotransmitters which plays a significant role in the function of human metabolism, hormonal, cardiovascular and central nervous systems. Several diseases and neurological disorders such as Parkinson's disease, schizophrenia and Huntington's disease can be caused due to deficiency of dopamine. Therefore lower concentration detection of dopamine in biological samples such as sweat and/or urine containing dopamine metabolites is very crucial. In this study, we propose cerium oxide coated polymer nanopillars based sensor to achieve lower limit detection of dopamine with high sensitivity and selectivity for diagnostic applications. Cerium oxide nanoconstructs (nanoceria) that have the potential to act as antioxidant attributed to its switching of oxidation state from +3 to +4 mediated at the oxygen vacancies. The unique inter action between dopamine and the redox active nanoceria is studied using *in-situ* UV-visible spectro-electrochemistry and surface characterization methods. It has been previously observed that there is a strong attachment of dopamine to nanoceria surface through oxidation followed by formation of a charge transfer complex, there by motivating to develop a sensor to detect dopamine. In this study, cerium oxide is immobilized on high aspect ratio nano-pillars made of polyacrylonitrile polymer. The nanopillars fabricated using soft lithography increased the surface area of exposed cerium oxide, thereby increasing the interaction of the nanoparticles with dopamine. The changes in the redox potential and surface chemistry of cerium oxide coating upon reaction with dopamine were recorded using electrochemical and optical techniques. Cerium oxide coatings were obtained using different techniques such as sputter coating, atomic layer deposition, electrodeposition and spin coating to obtained different surface chemistry (ratio of Ce^{3+}:Ce^{4+} on the surface) to improve the detection limit of the dopamine.

AS-TuP28 X-ray Photoelectron Spectroscopy of Raw Material for Metal Additive Manufacturing*, David Wieliczka,* *A.S. Choi, J.A. Crow, C.J. Cook, L.F. Elder, R.D. Koch, T.A. Pond, B.C. Sartin, D.R. Shinault, S.E. Van Slyke,* Honeywell Federal Manufacturing and Technology

Understanding the effects of powder reuse on metallurgical properties of components fabricated via laser powder bed fusion is critical to ensure the production of functional components. The inability to reuse metal AM powder will have a significant negative economic impact on this manufacturing method. In mid-2015, the KC NSC initiated a 316L powder

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[*] **National Student Award Finalist**

study on a consistent run of components. This paper will present surface analysis results from both virgin metal powder and powder sampled from the overflow bin after a build. In addition to XPS, the powders have been examined with SEM/EDS to provide morphology and composition, direct probe mass spectroscopy to examine the outgassing of the material, and ICP-MS to examine the impurities at ppm levels. The XPS data was obtained from the surface of the powder as well as a function of depth utilizing argon ion sputtering and provides unique information on the elemental composition of the surface. Specifically, we were tracking the elemental surface enrichment due to vapor created during the build process. We are also examining the oxide chemistry of both the surface and near surface region.

AS-TuP29 Characterization of Bonding between Super-hard Ceramics and Polymer Substrate*, **Ranganathan Parthasarathy**,* Tennessee State University*; JB. Beam,* Vanderbilt University*; FEH. Hoff,* Tennessee State University*; A. Misra,* University of Kansas*; L.Z. Ouyang,* Tennessee State University*; CML. Lukehart,* Vanderbilt University

Superhard coatings improve the durability of biomedical polymer implants due to their excellent wear resistance. We study the bond strength between Rhenium Diboride (ReB_2), a superhard ceramic, and Teflon, which is widely used as an implant material in load-bearing biomedical applications. As part of a proof-of-concept study, ReB_2 is coated onto Teflon using confined-plume chemical deposition at room temperature and pressure. For the coating to function effectively in load-bearing conditions, the bond strength between the polymer and the coating must well exceed in-situ stresses. Accurate local measurement of bond strength using nano-indentation is difficult owing to platelet microstructure of the ReB_2; hence an experimental workflow was designed to determine the average macro-scale bond strength between Teflon substrate and ReB_2 coating. The inert nature of Teflon makes conventional pull-out challenging. Therefore, we performed a)Tensile pull-out of the deposited ceramic coating based on a modified version of ASTM D4541, b) Imaging of failure surfaces using light microscopy and Scanning Electron Microscopy (SEM) c) Image segmentation to determine area of failure, and d) Calculation of average stress at pull-out. The tests reveal average bond strength of 2.5 MPa between Teflon and ReB_2 for coatings deposited on an untreated Teflon surface and 4.5 MPa for those on a sanded and etched Teflon surface. The pull-out occurs in a brittle manner, with no observable yield or plastic flow. The SEM images reveal strands of Teflon on the pull-out side, indicating that the true bond strength is likely higher than the measured average. Imaging of the Teflon surface under the coating reveals that the confined-plume chemical deposition creates a laminate surface of ReB_2 on the substrate, as opposed to anchored platelets. The results confirm the development of a robust and repeatable workflow for the measurement of average bond strengths of super-hard ceramic coatings on comparatively soft polymer substrates.

Applied Surface Science
Room 101B - Session AS+SS-WeM

Applications where Surface Analysis is Your Only Hope

Moderators: Jeffrey Fenton, Medtronic, Svitlana Pylypenko, Colorado School of Mines

8:00am **AS+SS-WeM1 Accurate Ion Beam Analysis of Electrolytes via Rutherford Backscattering (RBS) and Positive Ion X-ray Emission (PIXE) of Uniform Thin Solid film of Blood congealed via HemaDrop™**, ***Yash Pershad**, N.X. Herbots,* SiO2 NanoTech LLC*; C.F. Watson,* SiO2 NanoTech LLC/Arizona State University Physics Dpt*; EJ. Culbertson,* University of California at Los Angeles

Medical diagnostics needs new methods of blood analysis using mL of blood rather than the standard 7 mL to improve care. Theranos has been recently challenged about their "finger-stick method," where blood drops are used for complete blood diagnostics, not just glucose. They only approved by the FDA for qualitative detection, rather than accurate blood composition. Motivated by these accuracy issues, along with the great need for diagnostics from microliters of blood, we use MeV Rutherford Backscattering Spectrometry (RBS) to measure elemental composition (H, C,N, O, K, Mg, Ca, Na, Fe) in microliters of blood congealed into smooth, planar, Homogeneous Thin Solid Films (HTSF). These planar HTSF of blood are prepared with a new technology that congeal blood drops, called HemaDrop™ [1, 2] Measurements on HTSF prepared via HemaDrop™ are compared and found much more reproducible and accurate than those taken for comparison on dried blood drops, such as the so called "Dried Dlood Spot (DBS)" that can only be used in microvolume sampling for drug metabolism, not blood composition. HTSF prepared with HemaDrop™ yields reproducible elemental composition regardless of substrate used or area of analysis with < 6% sampling error. Ion damage from RBS is accounted for via the 0-dose intercept damage curve method, which graphs RBS yield of elements detected, as a function of analysis dose, using several sequential cumulative spectra. Positive Ion X-ray Emission (PIXE) is used to verify the reproducibility and accuracy of RBS. RBS and PIXE analysis on HTSF prepared with HemaDropTM using 6 microliter of blood are found in excellent agreement within the 6% sampling error. Thus, HemaDropTM successfully creates homogeneous thin solids film from blood that can be analyzed in vacuum and can also be used for Infrared (IR) spectroscopy and Tapping Mode Atomic Force Microscopy for molecular identification and counting. HTSF enable for the first time blood analysis via vacuum-based methods. IR and TMFAM are also being investigated to add molecular identification and counting.

[1] US Patent Pending, Assignee: SiO2 NanoTech, Inventors: Herbots, N, Watson CF, Krishnan A, Pershad Y, et al (2016)

[2] Electrolytes Detection by Ion Beam Analysis, in Continuous Glucose Sensors and in Microliters of Blood using a Homogeneous Thin Solid Film of Blood, HemaDrop™. Yash Pershad, Ashley A. Mascareno, Makoyi R. Watson, Alex L. Brimhall, Nicole Herbots, Clarizza F. Watson, Abijith Krishnan, Nithin Kannan, Mark W. Mangus, Robert J. Culbertson, B. J. Wilkens, E. J. Culbertson, T. Cappello-Lee, R.A. Neglia Submitted to MRS Advances, April 2016

8:20am **AS+SS-WeM2 Surface Analysis As a Valuable Tool to Study Chemistry of Metals in Environmental Problems**, ***Kateryna Artyushkova**,* University of New Mexico*; J. Blake,* New Mexico Water Science Center*; L. Rodriguez-Freire, S,. Avasarala, A. Ali, A. Brearley, E. Peterson, J.M. Cerrato,* University of New Mexico

This talk will present application of X-ray Photoelectron Spectroscopy to understand the role of chemistry of metals in several environmental problems. In the first study, the chemical interactions of U and co-occurring metals in abandoned mine wastes in a Native American community in northeastern Arizona were investigated using spectroscopy, microscopy and aqueous chemistry. Elevated concentrations of metals are of concern due to human exposure pathways and exposure of livestock currently ingesting water in the area. This study contributes to understanding the occurrence and mobility of metals in communities located close to abandoned mine waste sites. Elevated U (6,614 mg/kg), V (15,814 mg/kg), and As (40 mg/kg) concentrations were detected in mine waste solids. The power of XPS in specific identification of the chemical states of these elements as U (VI), As (-I and III) and Fe (II, III) will be presented.

In the second study, the goal is to investigate the effect of metals associated with wildfire ash from wood collected from the Valles Caldera National Preserve, Jemez Mountains, New Mexico on water chemistry. Metals and other constituents associated with wildfire ash can be transported by storm event runoff and negatively affect water quality in streams and rivers. Microscopy and spectroscopy analyses were conducted to determine the chemical composition of ash. Metal-bearing carbonate and oxide phases were detected through X-ray spectroscopy analyses.

Finally, we integrated spectroscopy, microscopy, diffraction, and water chemistry to investigate the presence of metals in water and sediment samples collected 13 days after the Gold King Mine spill (occurred on August 5, 2015). Spectroscopy, microscopy, and XRD analyses suggest that Pb, Cu, and Zn are associated with metal-bearing jarosite ($KFe^{3+}{}_3(OH)_6(SO_4)_2$) and other minerals (e.g. clays, Fe-oxides and oxyhydroxides) identified in sediments from Cement Creek, CO. The presence of sulfates and phosphates, Fe as 75% Fe^{2+} and 25% Fe^{3+}, and 100% Pb^{2+} in the near surface region of these sediments was detectedby XPS analyses.

Additionally, phosphates and nitrogen species were found with XPS in the sediments from Farmington, NM, downstream the Animas River. The interaction of these metal-bearing minerals with biogeochemical processes occurring downstream could cause metal mobilization into the water.

8:40am **AS+SS-WeM3 Surface Analysis Techniques – Hope Springs Eternal**, ***John Newman**, S.R. Bryan, D.M. Carr, G.L. Fisher, J.S. Hammond, J.E. Mann,* Physical Electronics USA*; T. Miyayama,* ULVAC-PHI, Japan*; J.F. Moulder, D. Paul,* Physical Electronics USA*; R. Inoue,* ULVAC-PHI, Japan*; B. Schmidt,* Physical Electronics USA **INVITED**

In today's technologically advanced laboratories there are many dozens of different, and very specialized, analytical techniques being used to attempt to solve problems and characterize materials. When choosing the proper technique for a particular application, the needs of the study are matched to the attributes of a particular method – its depth of analysis, detection sensitivity, analytical spot size, type of information provided, and whether or not the technique is appropriate for the sample in question. For applications where the region of interest is measured in atomic layers, surface sensitive methods such as Auger Electron Spectroscopy, X-ray Photoelectron Spectroscopy, and Time-of-Flight Secondary Ion Mass Spectrometry have always been the methods of choice and, in most cases, really the only hope for a successful analysis.

However, when we look at the relatively recent technological advances in these three methods, we find that their increased capabilities expand their usefulness to much more than the traditional types of surface experiments. For example, gas cluster beams now allow for intact organic information to be obtained from depth profiles or cross-sectioned samples; higher energy x-ray beams allow for deeper analysis depths compared to traditional XPS x-ray beams; and tandem mass spectrometry technology can provide unambiguous peak identification in TOF-SIMS. This presentation will look at applications where some of these advancements are used; exemplifying how newer technologies are making these techniques our only hope for a much wider array of studies.

9:20am **AS+SS-WeM5 What Came First? The Black Ink or the Black Ink? That Is the Question**, ***Robyn E. Goacher**, L.G. DiFonzo, K.C. Lesko,* Niagara University

Determining the order of deposition of ink markings in questioned documents (forgeries) is an important forensic task. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has received attention as a possible technique for this purpose because it is a surface sensitive technique that can provide chemical images, potentially resolving the top ink from the bottom ink. Furthermore, static SIMS imaging is non-destructive, which is important for the preservation of unique evidence. Prior work demonstrated that ToF-SIMS can correctly determine deposition order of intersections between inks of dissimilar colors[1], and that the order of deposition between fingerprints and ink can be elucidated if the fingerprint is on top of the ink[2]. In order to further test the abilities and robustness of the method, intersections between similar inks need to be examined. In this study, three different black ink samples were tested (Bic^{TM}, Papermate^{TM}, and Staples^{TM} brand pens). Preliminary work produced inconsistent results, and indicated that a more thorough analysis of the primary ions striking the sample and of the polarity of the secondary ions collected needed to be done. Therefore, chemical images of the ink intersections were collected using $Ar\text{-}_{1000}^{+}$, Bi_3^+, and Bi_3^{2+} primary ions, with both positive and negative secondary ion spectra. Data were analyzed using Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR). Data analysis included consideration of regions of interest as well as full image analysis, with and without restrictions to the secondary ion mass range. The results point to issues regarding incorrect apparent order of deposition, potentially based on the interactions of inks of different types. This brings the forensic use of ToF-SIMS for determining the order of deposition in ink forgeries into question, and points to the need for further research on factors that can result in incorrect apparent deposition orders.

1. A. He, D. Karpuzov and S. Xu, "Ink identification by time-of-flight secondary ion mass spectrometry", *Surface and Interface Analysis,* **2006**, 38 (4), 854-858.

2. N.J. Bright, R.P. Webb, S. Bleay, S. Hinder, N. Ward, J.F. Watts, K.J. Kirby and M.J. Bailey. "Determination of the Deposition Order of Overlapping Latent Fingerprints and Inks Using Secondary Ion Mass Spectrometry", *Analytical Chemistry*, **2012**, 84, 4083-4087.

9:40am **AS+SS-WeM6 ToF-SIMS Analysis of Aerospace Topcoat Degradation***, **Taraneh Bozorgzad Moghim**, M.L. Abel, J.F. Watts,* University of Surrey, UK

Aircraft coatings are subjected to a multitude of environments during their service life time, including high humidity, extreme temperatures and solar radiation. The major source of degradation derives from ultra-violet (UV) radiation. With commercial aircrafts flying at altitudes between 9 and 13 km, their exposure to UV radiation and ozone significantly increases. Therefore photooxidation of an aircraft topcoat must be understood in order to monitor topcoat degradation. The main laboratory technique used to establish the degradation phenomena from UV radiation is through QUV chambers, however the effect of ozone is not considered in this method. The novelty of the approach used here, is in the use of a desktop cleaner, intended for SEM sample preparation, as the exposure method. This combines the effects of UV and ozone. The topcoat was subject to UV/ozone exposure for varying durations and analysed using time of flight-secondary ion mass spectrometry (ToF-SIMS).

The detail provided by ToF-SIMS is vital in understanding the degradation phenomena and enables a degradation mechanism to be established. ToF-SIMS produces a significant amount of data and therefore when combined with principal component analysis (PCA) a more detailed analysis of the data can be obtained. The main changes observed are the rise of inorganic components with exposure time, as the polymer resin decomposes and the inorganic pigments of the coating are exposed. However this does not describe the degradation of the organic components. Therefore by filtering out the inorganic contributions in the PCA, the changes to the organic components could be isolated and observed. This allows the positive identification of cluster ions of the reactants from the resin and those from the reaction products. In this manner it was possible to deduce the degradation mechanism.

11:00am **AS+SS-WeM10 Surface And Bulk: Are They Always The Same? X-Ray Photoelectron Spectroscopy Study***, **Tatyana Bendikov**, D. Barats-Damatov, B. Butschke, J. Bauer, J. Pellegrino Morono, T. Zell, R. Neumann, D. Milstein,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is a surface sensitive technique (top 10-15 nm) with sensitivity down to single atomic layer. XPS provides unique information about elemental composition and on the chemical and electronic state of the element in the material. The importance of XPS analysis is essential when the top surface and bulk of the material are different in chemical composition and, consequently, in their properties.

We present here two systems where XPS analysis shows significant differences in elemental composition of the top surface, compared to bulk material characterized by various analytical techniques, such as X-ray crystallography, NMR, EPR, Raman and infrared (IR) spectroscopies, etc.

In the first system, influence of temperature on the crystal packing and secondary structure of phosphovanadomolybdic acid, $H_5PV_2Mo_{10}O_{40}$ was studied.[1] After high temperatures treatment (400-600°C) XPS analysis reveals enrichment of the top surface of the $H_5PV_2Mo_{10}O_{40}$ by amorphous vanadate/phosphate layer.

In the second system, series of iron-PNN complexes were synthesized and characterized in terms of their stability, elemental composition and metal center oxidation state.[2-3] Using example of two complexes, $[(t\mathrm{BuPNN})\mathrm{Fe(NO)_2}]^+[\mathrm{BF_4}]^-$ and $[(t\mathrm{BuPNN})\mathrm{Fe(NO)}\text{-}_2]^{2+}2[\mathrm{BF_4}]^-$, PNN= 2-[(Di-tert-butylphosphinomethyl)-6-diethylaminomethyl)pyridine, it is shown by XPS study that NO ligands are not stable and easily escape from the complex. This reveals changes in structure and in paramagnetic/diamagnetic behavior of these complexes.

1. Barats-Damatov D., Shimon L.J., Feldman I., Bendikov T., Neumann R. *Inorg. Chem.***2015**, *54*, 628-634.

2. Zell T., Milko P., Fillman K.L., Diskin-Posner Y., Bendikov T., Iron M.A., Leitus G., Ben-David Y., Neidig M.L., Milstein D. *Chem. Eur. J.***2014**, *20*, 4403-4413.

3. Butschke B., Fillman K.L., Bendikov T., Shimon L.J., Diskin-Posner Y, Leitus G., Gorelsky S.I., Neidig M.L., Milstein D. *Inorg. Chem.***2015**, *54*, 4909-4926.

11:20am **AS+SS-WeM11 *In Situ* Chemical Imaging of Biointerfaces Using Microfluidics and Molecular Imaging***, **Xiao-Ying Yu**,* Pacific Northwest National Laboratory

The surfaces of aqueous phases and films 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, System for Analysis at the Liquid Vacuum Interface (SALVI), to enable direct observations of liquid surfaces and liquid-solid interactions using time-of-flight secondary ion mass spectrometry (ToF-SIMS). SALVI was recently applied to investigate biomolecules and biological interfaces in living biofilms and single mammalian cells. Specifically, a variety of hydrated protein thin films were studied, providing the first *in situ* observation of interfacial water or biological water. In the single cell study, ion transport through the ion channel in the cell membrane was mapped in wet cells. In our most recent biofilm research, characteristic fragments of the extracellular polymeric substance (EPS) were obtained for the first time, including proteins, polysaccharides, lipids, polymers, and distinct biomarkers. These species are useful to track the metabolic and electron transfer processes in the microbial communities. For example, biomarkers characteristic of quorum sensing as a result of biofilm response to environmental stressors such as $Cr_2O_7^{2-}$ exposure and subsequent dispersion of the biofilm can be observed using this novel approach. Correlative imaging was employed to achieve a more holistic view of complexed biological systems across different space scales. In addition, electron transfer mechanisms of living biofilms as the electrode material are being studied using the electrochemical version of our microfluidic reactor. Our results demonstrate that interfacial chemistry involving important biomolecules and biological systems can be studied from the bottom up all based on microfluidics. Our transferrable microfluidic reactor sets the analytical foundation toward chemical imaging of complex phenomena occurring in multiple time and length scales, or the mesoscale, underpinning chemical changes at the molecular level in the condensed phase.

11:40am **AS+SS-WeM12 Capturing the Transient Species at the Electrode-Electrolyte Interface by SALVI and Liquid ToF-SIMS***, **Jiachao Yu**, Y. Zhou, X. Hua,* Pacific Northwest National Laboratory*; S. Liu,* Southeast University, China*; Z. Zhu, X.-Y. Yu,* Pacific Northwest National Laboratory

In situ time-resolved identification of interfacial transient reaction species were captured using imaging mass spectrometry, leading to the discovery of unexpected and more complex elementary electrode reactions and providing unprecedented understanding of the reaction mechanism on the electrode surface and solid-electrolyte interface using dynamic molecular imaging. This unique approach was enabled by a vacuum compatible electrochemical microfluidic reactor, namely System for Analysis at the Liquid Vacuum Interface (SALVI). The chemical mechanism of iodine oxidation at the electrode surface was revisited using simultaneous cyclic voltammetry (CV) and dynamic ToF-SIMS. Our dynamic ionic and molecular imaging results suggested that more complex surface reactions exist concerning the gold adlayer formation on the electrode surface, providing the discovery of more short-lived transient species and new insights of elementary electrode reactions unknown in the textbook. Such findings further illustrated the importance of truly observing electron transfer reactions in real-time with high spatial chemical mapping. This innovated approach is suitable for fundamental kinetic studies in electrochemistry at the solid-liquid (s-l) interface or the solid-electrolyte interface with many potential applications such as energy storage, material conversion, and electrocatalysis. The ability to capture and elucidate complex reaction mechanisms at the dynamic s-l interface opens a new door to control, mitigate, design, and engineer reactive pathways toward predictive material synthesis, efficient energy storage, and favorable catalytic conversion.

12:00pm **AS+SS-WeM13 Energy Storage Materials – Investigating the Surface***, **Jonathan Counsell**, S.J. Coultas, C.J. Blomfield,* Kratos Analytical Limited, UK*; C. Moffitt,* Kratos Analytical Limited

Lithium ion batteries are commonly found in home electronic equipment. In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. Novel materials have been developed to also increase the energy storage density. Lithium phosphorus oxynitride (LiPON) has become the most commonly used solid electrolyte thin-film in energy storage devices. Obviously due to the widespread use of this material there is significant interest in understanding the characteristics and properties with a view towards optimisation.

Here we apply XPS and UPS to explore both the surface and bulk properties of several LixPOyNz surfaces prepared via atomic layer deposition ALD [1]. The distribution of elements below the surface is explored via ion and angular-resolved depth profiling methods. This technique has been used extensively across a broad range of applications however the damage caused by impinging ions on the structure of the analysis material has always been a concern for the analyst. More recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials and broaden the range of materials amenable to this type of analysis. Here we extend the application of cluster ions beyond organics to inorganic oxides. Herein we discuss how, with the use of Ar250-3000+ ions, where the energy per atom can be 2.5-40 eV, it is possible to obtain more accurate information regarding the true nature of the LiPON thin-film. A comparison is made with conventional monatomic depth profiles in particular the differences in stoichiometry obtained with the two ion sources. Ion implantation is also discussed as are the unfortunate chemical effects of carbon deposition from organic cluster ions. We will demonstrate how the analyst can now confidently depth profile through inorganic metal oxide thin-films without the worry of reduction or preferential sputtering.

[1] Alexander C. Kozen, Alexander J. Pearse, Chuan-Fu Lin, Malachi Noked, Gary W. Rubloff, DOI: 10.1021/acs.chemmater.5b01654

Surface Science
Room 104E - Session SS+AS-WeM
Environmental Interfaces, Ambient Surfaces, and In-Operando Studies

Moderator: R. Scott Smith, Pacific Northwest National Laboratory

8:00am **SS+AS-WeM1 In-situ Electron Microscopy of Synthesis, Chemistry and Self-assembly of Colloidal Nanostructures*, Eli Sutter,*** University of Nebraska - Lincoln **INVITED**

In-situ microscopy, particularly real-time imaging of dynamic processes has developed into an active field of research and is expected to be one of the key enabling techniques for understanding the formation of nanostructures, catalytic reactions, phase transformations, self-assembly, and other central issues in nanoscience and technology. *In-situ* transmission electron microscopy can be used to follow the behavior and measure the properties of nanostructures over a wide range of environmental conditions with resolution down to the atomic scale. While processes at variable temperatures and gas-solid interactions have been accessible for some time, observations in liquids have emerged only in recent years with the development of special membrane cells. Liquid-cell electron microscopy has developed into a powerful technique that allows the imaging of various processes in wet environments, such as liquids, solutions, or colloidal suspensions, and the investigation not only of a wide range of inorganic nanoscale objects but of biological systems as well.

I will illustrate the power of liquid-cell electron microscopy applied to imaging colloidal synthesis (nanoparticles, core-shell structure), electrochemistry (galvanic replacement reactions) and the self-assembly of nanocrystal superstructures in solution. Our results demonstrate that real-time electron microscopy can substantially advance our understanding of a wide range of processes involving nanoscale objects in bulk liquids.

8:40am **SS+AS-WeM3 Low Energy Electron Microscopy at Near Ambient Pressures*, Andreas Thissen,*** SPECS Surface Nano Analysis GmbH, Germany

Low-energy electron microscopy (LEEM) is a spectromicroscopy technique, which allows the study of dynamic processes at surfaces and interfaces, such as thin-film growth, surface reactions, and phase transitions. With the FE-LEEM P90 from SPECS, which is based on the instrument design by Rudolf Tromp from IBM [1,2], lateral and energy resolution of below 5 nm and 250 meV, respectively, can be achieved. Depending on the excitation source and the settings on the instrument a variety of different imaging modes are possible: mirror electron microscopy, low energy electron diffraction (LEED), phase contrast imaging, reflectivity contrast, dark field imaging and bright field imaging, as well as photoelectron emission microscopy and spectroscopy.

We have enhanced the technical capabilities of the FE-LEEM P90 towards studies under near ambient conditions by developing a special sample geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation.

9:00am **SS+AS-WeM4 Probing Liquid-Vapor Interfaces of Ionic Solutions with Lab-based APXPS*, John Newberg,*** *C. Arble, Y. Khalifa, A. Broderick, S. Rani,* University of Delaware

Ionic interfaces are ubiquitous in physical, chemical, biological, environmental and technological processes. Herein we will present recent efforts examining ionic liquid and deliquescent salt interfaces using lab-based ambient pressure X-ray photoelectron spectroscopy (APXPS) in the presence of water vapor. The onset to water uptake into the top few nm of a hydrophilic ionic liquid is surprisingly similar to hydrophilic solid surfaces. A hydrophilic salt zinc bromide was also probed as it transitions from a solid to a liquid. It will be shown for ionic solutions that the uptake of water leads to variable shifts in the binding energy of anion and cation moieties driven by their interaction with water.

9:20am **SS+AS-WeM5 Effect of Surface Passivation on Stability of Methylammonium Lead Iodide Perovskite***, Q. Peng,* ***Xiaozhou(Joe) Yu,*** University of Alabama

Methylammonium Lead Iodide Perovskite ($MAPbI_3$) is a promising photoelectronic material for various applications. However, the stability of $MAPbI_3$ is a big concern for its applications in outdoor application environments. Its stability is affected the interfaces between $MAPbI_3$ and other layers of materials, temperature, moisture, and O_2. Currently the detail decomposition mechanism is not clear yet. In this presentation, we will employ a suite of in-situ characterization methods including in-situ Fourier Transform Infrared spectrometer, quartz crystal microbalance, and quadrupole mass spectrometer to understand the decomposition mechanism when expense $MAPbI_3$ to different simulated application environments (such as Fig. 1). The effect of various surface passivation methods on the stability of $MAPbI_3$ will be presented to help illustrate the mechanism that govern the stability of $MAPbI_3$.

9:40am **SS+AS-WeM6 STM Reveals the Formation of Near-Ideal Self Assembled Monolayers on TiO_2 in Air and Solution*, William DeBenedetti,*** *M.A. Hines, E.S. Skibinski, A. Song, A. Ortoll-Bloch,* Cornell University

The surface chemistry of TiO_2 in air and solution is an important, but under-studied, topic for next-generation photovoltaics, environmental remediation, and CO_2 photoreduction. Using scanning tunneling microscopy (STM), polarized infrared spectroscopy and other techniques, we will show that surprisingly stable, near-ideal organic monolayers spontaneously form on rutile (110) in a variety of environments.

First, we will show that under ambient conditions, the rutile (110) surface is terminated by a monolayer of bicarbonate, HCO_3, and H formed from the reactive adsorption of CO_2 and H_2O — a reaction that has never been observed in ultrahigh vacuum. Contrary to conventional wisdom, this bicarbonate monolayer displaces H_2O bound to the surface, remaining intact even in vacuum up to ~700 K. The spontaneous formation of a HCO_3 monolayer has important implications for the mechanism of CO_2 photoreduction on TiO_2.

Second, we will show that near-ideal organic monolayers form when rutile (110) is immersed in a variety of aqueous solutions. As an example, highly ordered benzoate monolayers with a characteristic "paired" geometry can be formed from aqueous solutions. Using polarized infrared spectroscopy, we show that this pairing is not due to dimerization, as suggested by previous researchers. Instead, DFT simulations confirm that π-π interactions lead to long-range ordering and a tetrameric bonding geometry. The structure of these monolayers is further confirmed by disrupting the π-π interactions using a variety of fluoro-substituted precursors.

11:00am **SS+AS-WeM10 Study of the Electrical Double Layer of Calcium Carbonate Minerals*, Yijue Diao,*** *R.M. Espinosa-Marzal,* University of Illinois at Urbana-Champaign

Understanding the interactions taking place at the calcite-solution interface is crucial to elucidate many natural geochemical processes on or near the Earth's surface, such as biomineralization and CO_2 sequestration capture of inorganic contaminants by minerals, and enhanced oil recovery. Being the most stable crystalline phase of calcium carbonate, and one of the most abundant minerals, calcite has been studied intensively at the microscale. However, when it comes to the nanoscale, little is known about the molecular details of the calcite-solution interface. Not until recently have experimental and computational works, including our previous force spectroscopy studies, shown that unlike the conventional model of Stern layer, the calcite interface in aqueous phase is well defined by two layers of water molecules on top of which loosely bound hydrated calcium ions are located. Our previous work by colloidal probe atomic force microscopy (AFM) reveals the influence of confinement on the calcite surface under equilibrium conditions.

In this study, AFM with both a microsphere and a sharp tip is employed to perturb the electrical double layer (EDL) of calcite. By performing force measurements with a short interval that does not allow the EDL reaching equilibrium between consecutive force measurements, we perturb the EDL and afterwards scrutinize the kinetics of EDL re-formation. It has been shown that the calcite interface can be tuned by varying calcium concentration and hence, the influence of calcium concentration on the kinetics of EDL formation is also studied. On the other hand, we directly probe into the behavior of the Stern layer by resolving the film thickness transitions (FTTs) that result from squeezing-out layers of molecules confined between the tip and calcite. The significant difference in the confined area, which therefore induces confinements of different extent between the colloidal probe and the sharp tip, allow understanding the influence of the confinement on the EDL.

Calcium carbonate is stored in nanopores of marine organisms and of rocks. Knowing the nanoconfined interfacial structure of calcite from our previous study, we take one step further in this work to investigate the kinetics of the EDL formation under the perturbation induced by consecutive confinement, which allows us not only to spatially elucidate the calcite-solution interface, but also with time resolution.

11:20am **SS+AS-WeM11 Observation of Water Adsorption Structures on Ultrathin ZnO/Au(111)**, ***Junseok Lee***, *D.C. Sorescu, X. Deng,* National Energy Technology Laboratory

Adsorption of water at the nanostructured metal oxide surfaces has implications in catalysis and serves as a prototypical system in studying water-oxide interfaces. In this work, the adsorption of water on ultrathin ZnO nanostructures grown on Au(111) substrate is investigated using scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. Water overlayers are grown on well-defined monolayer and bilayer of ZnO nanostructures. STM images of water overlayer structures on the monolayer and the bilayer of ZnO nanostructures at low temperature are analyzed in detail at different water coverages with the help of DFT calculation results. Moire pattern is found to influence the adsorption structure of water on the ZnO nanostructure surfaces and the brightness of the Moire pattern of the ZnO structure is observed to be significantly modulated by the adsorption of water molecule. Various hydrogen bonded water network structures are observed on ZnO bilayer after desorbing excess water molecules. The edge of the ZnO monolayer is found to be decorated by water molecules up to room temperature but there was no evidence of adsorption of water at the edge of ZnO bilayer.

11:40am **SS+AS-WeM12 Surface and Bulk Crystallization Kinetics of Amorphous Solid Water Nanoscale Films**, ***Chunqing Yuan***, *R.S. Smith, B.D. Kay,* Pacific Northwest National Laboratory

We investigate the crystallization kinetics of nanoscale amorphous solid water (ASW) films using temperature-programmed desorption (TPD) and reflection absorption infrared spectroscopy (RAIRS). ASW is a metastable form of water created by vapor deposition on a cold substrate (T<130 K). We directly measure the surface (using TPD) and bulk (using RAIRS) ASW crystallization kinetics as a function of film thickness and temperature. The results show that nucleation and crystallization begins at the ASW/vacuum interface and then the crystallization growth front propagates linearly into the bulk. The linear propagation is further confirmed by adding a thin layer of isotopic D_2O ice indicator at different positions in the ice. These results show that the closer the isotopic layer is to the vacuum interface, the sooner the isotopic layer crystalizes, which confirms the top-down propagation of the crystallization front. Further evidence for ASW/vacuum interface nucleation mechanism comes from experiments where a decane layer is deposited on top of the ASW film. The presence of the decane layer impedes surface nucleation and dramatically decreases the crystallization rate. By separating surface nucleation and bulk propagation processes, we are able to extract the nucleation and growth rates of ASW crystallization between 140-160 K.

This work was supported by the US Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences & Biosciences. The research was performed using EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory, which is operated by Battelle operated for the DOE.

12:00pm **SS+AS-WeM13 Capture of Hyperthermal Atoms and Molecules by Amorphous Water Ice via Ballistic Embedding**, ***Grant Langlois***[*†], *S.J. Sibener,* University of Chicago

We present comprehensive work detailing the capture and aggregation of hyperthermal atoms and molecules (CO_2, CF_4, Xe, Kr) by amorphous solid water (ASW) under ultra-high vacuum conditions at 125 K, near the amorphous/crystalline transition. Using time-resolved *in situ* reflection-absorption infrared spectroscopy (RAIRS), the gases prepared in supersonic molecular beams with translational energies above ~3.0 eV are observed to directly embed underneath the vacuum-ice interface to become absorbed within amorphous ice films despite an inability to adsorb at 125 K. Embedding into crystalline films, when observed, is less effective. Upon embedding, resultant mobility within the ice and the strength of intermolecular interactions can yield segregation of these gases into clusters, as seen in the case of CO_2. Tracing the kinetics of these embedding events under different energetic conditions allows for elucidation of the underlying dynamics, and we draw comparison between all studied gases to promote generalized conclusions in regards to empirical prediction of embedding probability. Through application of a classical model of the entrance barrier for atoms and molecules colliding with amorphous ice, we provide direct evidence for a unified connection between embedding probability and momentum of the incoming atoms and molecules; an account of all embedding data measured by our group traces a singular barrier. This work highlights the interplay between translational energy and momentum accommodation during collisions with ice; atoms and molecules can become trapped in an icy surface despite an inability to simply stick to the interface. These results are of considerable importance to studies of both the astrochemistry and evolution of interstellar bodies and dust, and detailing the capture and release of gases by permafrost relating to global climate forcing.

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

[†] **National Student Award Finalist**

Applied Surface Science
Room 101B - Session AS-WeA

Multiple Technique Approaches for Real-World Industrial Problem Solving

Moderators: Kateryna Artyushkova, University of New Mexico, Xia Dong, Eli Lilly and Company

2:20pm **AS-WeA1 Integrated XPS/ Raman Spectroscopy for Comprehensive Structural, Molecular and Chemical Surface Analysis***, **Christopher Deeks**, P. Mack, T.S. Nunney, J.P.W. Treacy, M. Meyer, N. Hibbard,* Thermo Fisher Scientific, UK

Advanced materials present ever increasing challenges to the analytical scientist. Composite materials built from nanostructures or ultra-thin films, often with complex chemistries present, are now required in a broad range of applications, and achieving full characterization is rarely managed using only one analysis method. To maintain confidence in the results from the utilization of several different methods, it is advantageous to be able to perform experiments on the same platform. Ideally, this should be without having to move the sample, removing the need for additional registration or processing to ensure that the data is being collected from the same position.

Often in surface analysis many related techniques are integrated onto the same system. These can include such practices as Ultraviolet Photoelectron Spectroscopy (UPS) for valence band and work function measurements. Ion Scattering Spectroscopy (ISS) is often used to give much more elemental surface information compared to XPS alone. Reflected Electron Energy Loss Spectroscopy (REELS) can also give information on hydrogen in samples which cannot be detected by any of the previously named techniques, allowing full elemental analysis of samples with these combined.

An integrated system that has a Raman spectrometer with a micro-focused, monochromated XPS system can be used for even further analysis. The focal points are aligned such that data can be acquired from the same point simultaneously, and that the sizes of the analysis areas are comparable in size. This combined approach is particularly powerful when analyzing carbon nanomaterials. Chemical modifications of the material can be easily determined and quantified with XPS, and Raman offers a fast way of determining the quality and conformity of the material. Vibrational structure can also give more precise chemical information in some cases. The greater depth of field of the Raman spectrometer also offers bulk information to complement the surface sensitive XPS data.

In this presentation we will discuss the strengths of this combined, in-situ approach to surface analysis, illustrated with examples from a range of applications including carbon nanomaterials, microelectronics and geology.

2:40pm **AS-WeA2 Extended Molecular Identification with TOF-SIMS Imaging MS/MS***, **John Hammond**, G.L. Fisher, S.R. Bryan,* Physical Electronics*; S. Iida, T. Miyayama,* ULVAC-PHI, Japan

TOF-SIMS has become widely accepted as the most powerful spectroscopy and imaging surface analysis tool for organic and polymer samples based on the capabilities of 2 nm surface sensitivity and 100 nm spatial resolution. For most polymer additives as well as lipids, disease markers and fatty acids on biological tissue samples, the molecular ions have masses up to m/z 1000. At this higher mass range, traditional TOF-SIMS lacks the mass resolution and mass accuracy to uniquely identify the detected ions. A new TOF-SIMS instrument combining, in parallel, imaging MS and imaging MS/MS provides the capability to provide a multi-technique approach to real world problem solving with extended molecular identification of higher mass ions [1].

A series of saturated and unsaturated fatty acid standards as well anti-oxidant polymer additives were analyzed with a PHI *nanoTOF* II TOF-SIMS Parallel Imaging MS/MS. The MS/MS spectra were generated with a 1 daulton precursor selection window followed by 1.5 keV collision-induced dissociation (CID). The MS^1 and MS^2 parallel imaging of polymer surfaces with a mixture of polymer additives were obtained with a raster scanned Bi_3^+ ion source with a sub-micron spatial resolution

The structural elucidation of the fatty acid CID MS/MS spectra can be interpreted by charge-remote fragmentation [2]. The location of unsaturated bonds in the fatty acids can be defined from these spectra. The complex structures of the anti-oxidants can be easily identified with the high energy CID MS/MS. Using the high signal/background of the MS^2 images, bunched or unbunched imaging with the Bi_3^+ ion source can produce sub-micron spatial resolution with unique molecular identification of additives on the polymer films. These results also point to a broader utility of this technique for biological tissue imaging.

4. References

[1] P.E. Larson, J.S. Hammond, R.M.A. Heeren, G.L. Fisher, *Method and Apparatus to Provide Parallel Acquisition of MS/MS Data*, U.S. Patent 20150090874, 2015.

[2] M. L. Gross,, Int. J. Mass Spectrom., 200 (2000) 611

3:00pm **AS-WeA3 Practical Aspects of Multiple Technique Problem-Solving: Making it Work***, **Kathryn Lloyd**,* DuPont Corporate Center for Analytical Sciences **INVITED**

Although there do exist types of problems or research support for which one analytical technique is sufficient to provide useful guidance or an answer, it is more the norm that multiple analytical techniques are required to address technical problems involving coatings, layered structures, and other industrial materials. In fact, basing action (e.g., a change in manufacturing process) on data from a single analytical technique -- especially a surface-specific technique – would not be advisable in most cases.

Some technique combinations seem intuitive – for example, combining the high-lateral-resolution detail from electron microscopy with the higher level of chemical information available from either secondary ion mapping (ToF-SIMS) or Raman microprobe analysis. However, there are still challenges with sample preparation, data acquisition from the same area, and data integration that need to be addressed.

Other technique combinations arise from the business need – for example, finding a combination of techniques that both describe the chemistry and correlate with end-use performance. This usually involves combining a vacuum-based technique with an ambient or “macroscopic” technique such as contact angle, porosity, or friction measurements.

As most practitioners know, the surface specificity of XPS and ToF-SIMS can be both an advantage and a disadvantage. In this regard, the introduction of GCIB (Gas Cluster Ion Beam) sources has opened up new opportunities for multiple-technique problem-solving.

This talk will present some experiences and examples that provide a flavor of multiple-technique problem-solving in an industrial environment.

4:20pm **AS-WeA7 Adhesion Aspects of Polymeric Methylene Diphenyl Diisocyanate on Different Steel Surfaces by XPS and ToF-SIMS***, **Jorge Bañuls Ciscar**, M.L. Abel, J.F. Watts,* University of Surrey, UK

Polymeric methyl diphenyl diisocyanate (p-MDI) is a versatile isocyanate commonly used in coatings and adhesives applications because of its excellent mechanical properties. In this work, we are aiming to understand the chemistry involved at the interface between p-MDI and a specific stainless steel as a result of different processing parameters. This steel has distinct surface properties. On one side the surface has been ground and the composition is mostly iron oxide (Fe_2O_3) whereas on the other side the steel has a mill-finished surface and the composition is predominantly chromium oxide (Cr_2O_3). Therefore, in our system of interest, the stainless steel has different physical and chemical properties on each side. As such, understanding the adhesion aspects of p-MDI on each side could lead to an improvement of its use in many steel applications.

Preliminary work using XPS and ToF-SIMS has shown an interaction between nitrogen and chromium oxide at the interface. A low binding energy peak (~397 eV) was identified in the N1s high resolution XPS spectrum. This peak represents nitrogen atoms which have a higher electronic density as a result of the electron withdrawing effect of the MDI on the metal substrate. Additionally, peaks of characteristic fragments of N-Cr interaction were found in the ToF-SIMS spectra. This will form the basis of further work to determine the exact chemistry involved in such interfacial regions.

4:40pm **AS-WeA8 Migration of Erucamide in Polyethylene Films***, **Michaeleen Pacholski**, R. Sharma, J. Ngunjiri, K. Laughlin, M. Kapur, V. Kalihari,* The Dow Chemical Company

Polyolefins are often formulated with additives to provide stability and processability depending on their end use. Reduction of coefficient of friction (COF) for polyolefin films is a critical property. A common additive for COF reduction is erucamide. Films made using this fatty amide are known to have diminished COF performance when exposed to elevated temperatures that might be found in hot trucks or warehouses. Characterization of these materials during and after thermal aging can provide useful understanding in deterioration of film performance. Here we use a multitechnique approach to characterize the surface chemistry and morphology of this relatively simple, yet common, system of polyethylene and erucamide.

5:00pm **AS-WeA9 Probing the Impact of Process and Materials Variability of Medical Device Components with Surface Characterization***, **Jeffrey Fenton**, L. Nygren, B. Tischendorf, R. Jahnke, J. Heffelfinger,* Medtronic plc

Since the first pacemaker implant in 1958, engineering and medical advances have greatly improved device capabilities and patient outcomes. Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. This presentation will focus on the utilization of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) on processes related to two device components, feedthroughs and printed wire boards, as a means to improve processing conditions, expand processing boundaries, and understand failure modes.

In pacemakers or like devices, feedthroughs are evaluated using various electrical tests to determine the insulation resistance which is typically in the Megaohm or Gigaohm range. XPS and SEM analysis will be shown to aid in the determination of yield loss root cause by identifying sources of foreign materials. For example, fibers from clothing may deposit onto the insulator and graphitize during high temperature processes. The graphitized materials may then provide a pathway for conductivity during electrical testing. Compositional and morphological identification with SEM allows for root cause identification and elimination of those yield losses.

Laser soldering, which is relatively new to the industry, is utilized in new Medtronic products. During the laser soldering process localized heat results in a different wetting dynamic from the conventional furnace reflow. The laser soldering process may be used after preceding thermal exposure in the upstream processes resulting in changes to the surface condition of the soldering pads. The surface chemistry may change during thermal exposure which may cause reduced wettability and create one of the biggest challenges during the process development to overcome. XPS, SEM and XRF (x-ray fluorescence) methods provide key insight on the inter-diffusion between the metallization layers on the PBW and migration to the surface species that can limit pad solderability. The main outcome of the analysis was establishing design rules for the PWB plating, including metallization materials and layer thickness in multilayer metallization.

5:20pm **AS-WeA10 Multi-technique Characterization of PtNi Extended Surface Catalysts for Improvement of Electrocatalytic Activity and Durability***, S. Shulda, C. Ngo,* Colorado School of Mines*; S. Alia,* National Renewable Energy Laboratory*; J. Nelson Weker,* SLAC National Accelerator Laboratory*; B. Pivovar,* National Renewable Energy Laboratory*; **Svitlana Pylypenko**,* Colorado School of Mines

Transition metal nanowires are emerging as an effective structure for various heterogeneous catalysis applications. Metal and metal oxide nanowires have demonstrated high activity for the oxidative coupling of methane into higher value products, hydrogenation of aromatic compounds, and water splitting, among others. Of particular interest is the application of platinum-nickel and platinum-cobalt nanowires as oxygen reduction catalysts in polymer electrolyte membrane fuel cells (PEMFCs) as they have shown activities that significantly surpass the current state of the art Pt nanoparticles supported on high surface are carbon and are considered a promising alternative. The activity and durability of Pt nanowires is dependent on both the surface and bulk properties, which continuously evolve during different steps of the synthesis, electrode preparation, and fuel cells operation, making a multi-technique analysis approach necessary.

High surface area platinum nickel (PtNi) nanowires have been synthesized via spontaneous galvanic displacement. Various post-processing treatments were applied altering the chemistry and structure of the nanowires to improve their activity and durability. This work focuses on the analysis of the surface and bulk composition and structure and their evolution with various treatments. X-ray photon spectroscopy (XPS), energy dispersive x-ray spectroscopy (EDS) via transmission electron spectroscopy (TEM), x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopies, and transmission x-ray microscopy (TXM) were utilized. All of the processing treatments altered the surface chemistry and in some instances the morphology of the nanowires, with some treatments resulting in increased activity and durability while others being detrimental to the performance. The extensive characterization of the nanowires pre- and post-processing provided a robust understanding of each treatments effect on the nanowires and guided the optimization of the post-processing treatments. Moreover, this study highlights the challenges associated with the characterization of nanowires structures, where evolution of both surface and bulk composition and structure are extremely important.

5:40pm **AS-WeA11 Compositional Analysis for Additive Manufacturing***, **Michael Brumbach**, N. Argibay, D. Susan, J. Rodelas, J. Reich, B.L. Boyce, A. Roach,* Sandia National Laboratories

The implementation of characterization in additive manufacturing (AM) demands new perspectives for a setting traditionally adapted to support basic science research. As the development of AM continues, the need for diagnostics and control of AM processes is critical and begins with an understanding of materials composition. This exploration of characterization techniques for analyzing bulk composition will give particular consideration for low detection limits, high-throughput analyses, and the ability to quantify light elements. Comparisons between optical emission spectroscopy (OES) from various excitation sources including glow-discharge (GDS), arc-spark, and inductively coupled plasma (ICP) will be discussed. The results are compared to X-ray fluorescence (XRF) and wavelength dispersive spectroscopy (WDS/microprobe). Combustion analysis will be discussed for carbon, sulfur, oxygen, nitrogen, and hydrogen from traditional wrought metals and AM analogs. The role of surface analysis and comparison to bulk techniques will also be demonstrated.

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

6:00pm **AS-WeA12 Ambient Mass Spectrometry for the Analysis of Organic Monolayers***, **Han Zuilhof**,* Wageningen University, Netherlands

The characterization of organic monolayers is critically dependent on highly surface-sensitive methods. While a wide variety of methods has been developed over the last decades, *structural information* of organic species, including information relating to their three-dimensional structure, was often very difficult to obtain.

The current presentation sets out to detail the potential of ambient ionization mass spectrometry for this purpose, by giving examples of where it can extend the analysis, where e.g. XPS, scanning probe microscopies and IR fall short.

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Surface Science
Room 104D - Session SS+AS+EM-WeA
Semiconductor Surfaces and Interfaces

Moderator: Andrew Gellman, Carnegie Mellon University

2:20pm **SS+AS+EM-WeA1 Adsorption of Triethylenediamine on Si(100)-2×1 Surface via N-Si Dative Bonding and C-N Dissociation***, **Jing Zhao**, M. Madachik,* University of Delaware*; K. O'Donnell,* Curtin University, Australia*; O. Warschkow,* University of Sydney, Australia*; L. Thomsen,* Australian Synchrotron, Australia*; G. Moore, S. Schofield,* University College London*; A.V. Teplyakov,* University of Delaware

The functionalization of silicon surfaces with thin layers of organic materials is an important area of studies with current and potential applications in microelectronics, catalysis, and bio-sensing. Triethylenediamine (also known as 1,4-diazabicyclo[2.2.2]octane, or DABCO) presents an interesting case study for silicon functionalization because of its symmetric structure with two x nitrogen atoms in tertiary amine configuration. Each of these atoms could potentially form a dative bond with a clean Si(100)-2x1 surface while the other may remain accessible for further modification. We applied infrared spectroscopy (MIR-FTIR), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD) supported by density functional theory calculations (DFT) to investigate the reaction mechanism of triethylendiamine with a clean Si(100)-2×1 surface, focusing specifically on dative bond formation and C-N dissociation.

2:40pm **SS+AS+EM-WeA2 Chemoselective Adsorption of Functionalized Cyclooctynes on Silicon***, M. Reutzel, N. Munster, M.A. Lipponer,* Philipps-Universität Marburg, Germany*; C. Langer,* Justus Liebig University Giessen, Germany*; U. Hofer, U. Koert,* Philipps-Universität Marburg, Germany*;* ***Michael Durr,*** Justus Liebig University Giessen, Germany

The adsorption of organic molecules on silicon surfaces has been subject of intense research due to the potential applications of organic functionalization of silicon surfaces in semiconductor technology. The high reactivity of the silicon dangling bonds, however, presents a major hindrance for the first basic reaction step of such a functionalization, i.e., chemoselective attachment of bifunctional organic molecules on the pristine silicon surface. Due to the high reactivity of the dangling bonds, each functional group of a bifunctional molecule adsorbs with an initial sticking coefficient close to unity and thus the final adsorption product will typically consist of a mixture of molecules adsorbed via different functional groups.

We overcome this problem employing cyclooctyne as the major building block of our strategy. Using scanning tunneling microscopy and X-ray photoelectron spectroscopy, cyclooctyne derivatives with different functional side groups are shown to react on Si(001) selectively via the strained cyclooctyne triple bond while leaving the side groups intact. The origin of this chemoselectivity is traced back to the different adsorption dynamics of the functional groups involved. We show that cyclooctyne's strained triple bond is associated with a direct adsorption channel on the Si(001) surface, in contrast to most other organic molecules which adsorb via weakly bound intermediates. In these intermediate states, the molecules have a finite lifetime and are often mobile and free to rotate on the surface. This allows the bifunctional molecule to sample the surface with the strained triple bond during its finite lifetime in the trapped state and in consequence, bifunctional molecules with a strained triple bond as one functional group will end up with this group attached to Si(001) even if the initial interaction proceeds via the second functional group.

Chemoselectivity can thus be achieved even on the highly reactive Si(001) surface when exploiting the adsorption dynamics of the respective reaction channels.

3:00pm **SS+AS+EM-WeA3 Compositions, Structures, and Electronic Properties of Grain Boundaries of Cu(InGa)Se$_2$***,* ***Xudong Xiao,*** Chinese University of Hong Kong **INVITED**

Polycrystalline semiconductors are important energy materials and the grain boundaries play crucial role in their electrical transport property. While in general grain boundary is detrimental, for Cu(InGa)Se$_2$ (CIGS), it was found that the grain boundary is benign to the electrical transport and a record solar cell energy conversion efficiency of 22.3%, the best among all thin film solar cells, has been achieved with a polycrystalline film. This peculiar benign behavior has attracted great attention in the materials science community, unfortunately, even with tremendous effort, the mechanism of the benignity of CIGS grain boundary remains as an outstanding problem, mostly due to the lack of convincing experimental evidences.

We performed our study by design and prepare well controlled CIGS samples with two different Cu content. By careful treatment of the samples to remove artifacts, we used a combination of techniques, namely AFM, STM, and TEM, to probe at nanoscales the composition, structure, and electrical properties of the individual grain boundary in direct comparison to those of the individual grain interior. We discovered that the grain boundary in fact consists of a boundary layer of finite thickness in addition to the grain boundary surface/interface for the non Σ3 grain boundaries. This boundary layer has a definitive composition, structure, and electronic band, independent of the overall Cu content in the CIGS films. The observation of similar grain interior and similar grain boundary except the boundary layer thickness for the two samples with very different overall Cu content is indeed a surprising finding that has never been reported before. The band alignment between grain boundary and grain interior was discovered to be of type II with downward offset for both conduction and valence bands at grain boundary, well correlating to the local copper deficiency and structure. Our findings expressively support the type inversion and large hole barrier in this grain boundary layer, and establish a comprehensive mechanism for the suppression of carrier recombination therein.

4:20pm **SS+AS+EM-WeA7 Thermal Self-limiting CVD Silicon and ALD Silicon Nitride Containing Control Layers on $In_{0.53}Ga_{0.47}As$(001)-(2x4), $Si_{0.5}Ge_{0.5}$(110), and $Si_{0.7}Ge_{0.3}$(001)***,* ***Steven Wolf****, M. Edmonds, T. Kent, K. Sardashti,* University of California at San Diego*; M. Chang, J. Kachian,* Applied Materials*; R. Droopad,* Texas State University*; E. Chagarov, A.C. Kummel,* University of California at San Diego

Compound semiconductors with high mobilities such as InGaAs and SiGe are being employed in metal oxide semiconductor field effect transistors (MOSFETs) to increase transistor performance. However, these surfaces contain dangling bonds that can affect the surface Fermi level; thus, depositing a control layer via ALD or self-limiting CVD on multiple materials and crystallographic faces is required . Silicon uniquely bonds strongly to all crystallographic faces of $InGa_{1-x}As$, $In_xGa_{1-x}Sb$, $In_xGa_{1-x}N$, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which can then be passivated by atomic hydrogen. Subsequently, the surface may be functionalized with an oxidant such as HOOH in order to create a terminating Si-OH layer, or a nitriding agent such as N_2H_4 in order to create an Si-N_x diffusion barrier and surface protection layer. This study focuses on depositing saturated Si-H_x and Si-OH seed layers via a self-limiting CVD process on InGaAs(001)-(2x4), and depositing a Si-N_x seed layer on $Si_{0.5}Ge_{0.5}$(110) and $Si_{0.7}Ge_{0.3}$(001) via an ALD process. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of these control layers on the various surfaces. A thin Si-H_x capping layer (2.5 monolayers) was deposited in a self-limiting CVD fashion on InGaAs(001)-(2x4) by exposing to Si_2Cl_6 at 350°C. This layer allows for multilayer silicon or Si-O_x growth by ALD through cyclically dosing Si_2Cl_6 with either atomic H or anhydrous HOOH. STM and STS measurements show the Si_2Cl_6 exposed InGaAs(001)-(2x4) surface is atomically locally ordered and has an unpinned surface Fermi level. Exposure to anhydrous HOOH at 350°C terminates the surface with Si-O bonds and does not lead to oxidation of substrate peaks. The HOOH treated surface then nucleates TMA at 250°C and ultimately further high-k gate oxide growth. MOSCAP device fabrication was performed on n-type InGaAs(001) substrates with and without a Si-H_x passivation control layer deposited by self-limiting CVD in order to determine the effects on $C_{max,}$ frequency dispersion, and midgap trap states. Deposition of a SiO_xN_y diffusion barrier and surface protection layer was achieved on the $Si_{0.5}Ge_{0.5}$(110) and $Si_{0.7}Ge_{0.3}$(001) surfaces via an ALD process at 275°C through cyclically dosing Si_2Cl_6 and anhydrous N_2H_4. MOSCAP device fabrication was performed on $Si_{0.7}Ge_{0.3}$(001) with and without a SiO_xN_y passivation control layer to compare device performance. Ultimately, the Si-H_x passivation layer gave less frequency dispersion at flat band and a lower D_{it}, and the SiO_xN_y passivation layer yielded lower gate leakage and D_{it} when compared to the respective wet clean only devices.

4:40pm **SS+AS+EM-WeA8 Formation of Atomically Ordered and Chemically Selective Si-O-Ti Monolayer on $Si_{0.5}Ge_{0.5}$(110) for a MIS Structure via H_2O_2(g) Functionalization***,* ***SangWook Park,*** *J.Y. Choi,* University of California, San Diego*; E. Chagarov,* Univeristy of California, San Diego*; B. Sahu, S. Siddiqui,* GLOBALFOUNDRIES*; N. Yoshida, J. Kachian,* Applied Materials*; A.C. Kummel,* University of California, San Diego

To overcome challenges when scaling down silicon-based complementary metal-oxide semiconductor (CMOS) devices, SiGe has received much attention due to its high carrier mobility and applications in strain engineering. Extremely thin oxides with appropriate band offsets can be utilized to form unpinned contacts on SiGe for a metal-insulator-semiconductor (MIS) structure. The TiO_2 interfacial layer on Ge is known to form a MIS structure which reduces the tunneling resistance due to the nearly zero conduction band offset (CBO) between TiO_2 and Ge. In this study, formation of TiO_x monolayer on SiGe(110) via H_2O_2(g) functionalization was investigated using *in-situ* scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS), and x-ray photoelectron spectroscopy (XPS). H_2O_2(g) was employed instead of the conventional H_2O(g) oxidant since H_2O_2(g) can form a uniform monolayer of –OH ligands on the surface without subsurface oxidation which should be ideal for forming the most stable possible interface which is a layer of Si-O-Ti bonds. STM verified that clean $Si_{0.5}Ge_{0.5}$(110) surfaces were terminated with both Si and Ge adatoms. STS measurements indicated that the Fermi level of clean $Si_{0.5}Ge_{0.5}$(110) surfaces was pinned near midgap between the valence and conduction band edges due to the half-filled dangling bonds of the adatoms. In order to passivate the dangling bonds, atomic H was dosed onto clean $Si_{0.5}Ge_{0.5}$(110) at 300°C which unpinned the Fermi level as demonstrated by STS. XPS analysis showed a saturation dose of H_2O_2(g) at 25°C left the $Si_{0.5}Ge_{0.5}$(110) surfaces terminated with a monolayer of both Ge-OH and Si-OH sites. STS indicated that the Fermi level on H_2O_2(g) dosed $Si_{0.5}Ge_{0.5}$(110) was shifted to near the valence band edge due to the formation of surface dipoles induced by hydroxyl bonds. Tetrakis(dimethylamido)titanium (TDMAT) or titanium tetrachloride (TiCl$_4$) was subsequently dosed onto hydroxyl-terminated Si$_{0.5}$Ge$_{0.5}$(110) at 25°C forming Ti bonds on surface. Both TDMAT and TiCl$_4$ dosed Si$_{0.5}$Ge$_{0.5}$(110) surfaces were annealed at 300°C and XPS verified that the Ti-O bonds were totally transferred from Ge atoms to Si atoms forming exclusively Ti-O-Si bonds on Si$_{0.5}$Ge$_{0.5}$(110) surfaces consistent with the strong bonding between Si and oxygen pulling Si atoms toward the surface to bond with oxygen while pushing Ge atoms into the subsurface during the annealing. STM demonstrated an ordered TiO$_x$ monolayer was formed with a row spacing which doubles the spacing of adatoms on clean Si$_{0.5}$Ge$_{0.5}$(110). In addition, STS indicated a TiO$_x$ monolayer on SiGe(110) was unpinned and therefore can serve as an ultra-thin insulating layer for a MIS structure.

5:00pm **SS+AS+EM-WeA9 The Effect of Ultrasonic Treatment (UST) on the Defect Structure of the Si–SiO$_2$ System**, ***Daniel Kropman**, T. Laas,* Tallinn University, Estonia

The effect of ultrasonic treatment (UST) on the defect structure of the Si–SiO$_2$ system by means of electron spin resonance(ESR),selective etching, MOS capacitance technique and secondary ions mass-spectroscopy is presented. The non-monotonous dependence of the defect densities on the US wave intensity has been observed. The influence of the UST frequency on the ESR signal intensity of the defect centres depended on the defects type and may be caused by vibration energy dissipation, which are a function of defect centres type. In the ESR spectra of Si samples a signal with g=1.9996 (Pa centres) connected with vacancy complexes is observed. After UST appears another signal with g=2.0055 (broken bonds of Si atoms). The influence of the US frequency and sample orientation on the ESR signal intensity varies for different centres. The frequency and orientation dependence of the ESR signal with g=l.9996 and the lack of this dependence for the centres with g=2.0055 show that vibration energy dissipation depends on the type of defect centers.Defect density at the interface grows with an increase of US wave intencity or changes nonmonotonously depending on the oxide thickness and crystallographic orientation. In the samples with thick oxide/0,6 mkm there is a maximum in the dependence of the charge carriers lifetime on the US wave amplitude and in the samples with thin oxides /0,3 mkm/ there is a minimum. This shows that the structural defects form electrically active centres and their density can be varied by US. The density of point defects and absorbed impurities at the Si–SiO$_2$ interface can be reduced and its electrical parameters improved by an appropriate choice of the UST and oxidation condition. US is widely used not only for materials treatment but in medicine as well (cancer treatment).

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5:20pm **SS+AS+EM-WeA10 Adsorption of C$_{60}$ Buckminster Fullerenes on a Carbon-free Hydrazine-modified Silicon Surface**, ***Fei Gao***[*]*, A.V. Teplyakov,* University of Delaware

Buckminster fullerene C$_{60}$ was used as a model to understand the attachment chemistry of large molecules on amine-terminated semiconductor surfaces. The resulting interface may serve as a foundation for devices in such fields as solar energy conversion, biosensing, catalysis, and molecular electronics. In this work, a monolayer of buckminster fullerenes C$_{60}$ was covalently attached to silicon surfaces using an efficient wet chemistry method. The starting chlorine-terminated Si(111) surface was initially modified with hydrazine to produce NH-NH functionality. Then the C$_{60}$ fullerenes were reacted directly with this surface. The chemical state and surface topography of the C$_{60}$-modified surface were characterized by surface analytical spectroscopic and microscopic methods, including X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), and atomic-force microscopy (AFM). The experimental results were also supported by computational investigation, density functional theory (DFT) calculations, that were performed to predict core-level energies of surface species formed and to propose the possible mechanism of surface reactions.

5:40pm **SS+AS+EM-WeA11 Passivation of SiGe Surfaces with Aqueous Ammonium Sulfide**, ***Stacy Heslop**, A.J. Muscat,* University of Arizona

Ge and SiGe are promising materials for future p-type metal-oxide semiconductor field effect transistors (MOSFETs) due to their higher hole mobilities and narrower bandgap compared to Si. In contrast to silicon, Ge and SiGe readily oxidize in ambient air forming nonstoichiometric Ge oxides that are detrimental to the electrical performance of the device. One approach is to remove these oxides and passivate the surface. SiGe with molar ratios of 25 and 75% Ge were treated with aqueous ammonium sulfide, (NH$_4$)$_2$S, to deposit sulfur. The composition of the surface was measured using x-ray photoelectron spectroscopy (XPS) as a function of concentration and pH. The (NH$_4$)$_2$S concentration was varied from 3 mM to 3 M, and the pH was varied from 10 to 8 using HCl and HF. Film thicknesses were measured with spectroscopic ellipsometry.

A fresh SiGe starting surface was produced by immersing in SC-1 (1:1:500 v/v) to form oxides and stripping the oxides using HF:HCl:H$_2$O (1:3:300 v/v). In the case of SiGe 25%, sulfides were not detected based on the S 2p XPS state for surfaces treated with (NH$_4$)$_2$S (Figure 1a). The oxygen coverage increased with increasing (NH$_4$)$_2$S concentration, forming primarily SiO$_2$ and a small coverage of GeO. The surface was enriched in Si and oxidized, and there was not enough Ge atoms exposed for S to bond to. HCl and HF were added to remove the Si and Ge oxides that formed. The addition of HCl and HF resulted in the deposition of sulfides on SiGe 25% (Figure 1b). The Si/Ge peak area ratio after oxide removal was 1.7. After immersion in 30 mM (NH$_4$)$_2$S at a pH of 10 the surface composition was unchanged (Si/Ge=1.7). For the same (NH$_4$)$_2$S concentration at a pH of 8 the surface was only slightly enriched with Si (Si/Ge=2.4). Overall, (NH$_4$)$_2$S is not an effective passivation reagent for Si-rich SiGe surfaces due to the lack of S deposited and the undesirable oxides which form during processing. By dropping the pH to 8, less than a monolayer of S is deposited but oxides still remain. In contrast, SiGe 75% did not oxidize as a function of the (NH$_4$)$_2$S concentration. Sulfur was detected based on the S 2p XPS state and the S coverage was independent of (NH$_4$)$_2$S concentration. The sulfur thickness increased from about 2.3 Å for (NH$_4$)$_2$S (30 mM or 1:100 v/v) at a pH of 10 to 3.4 Å for the same (NH$_4$)$_2$S dilution at a pH of 8 (Figure 1c and d). These film thicknesses were approximated from XPS peak areas based on a single layer model for S on Ge. The deposition of the S layer did not affect the surface stoichiometry between oxide removal steps (Si/Ge=0.19) and 30 mM passivation (Si/Ge=0.20).

6:00pm **SS+AS+EM-WeA12 Novel Electrical Circuit Model for the Design of InGaAs/GaAs (001) Strained-Layer-Super-Lattice**, ***Tedi Kujofsa**, J.E. Ayers,* University of Connecticut

Understanding lattice relaxation and dislocation dynamics has important implications in the design of highly functional and reliable semiconductor device heterostructures. Strain-layer-superlattices (SLSs) have been commonly used as dislocation filters whereby threading dislocations (TDs) can be removed by the insertion of a series of mismatched interfaces. The reduction of the threading dislocation in SLSs can be explained by the bending over of TDs associated with misfit segments of one sense by misfit dislocations having the opposite sense. Furthermore, the use of multilayered metamorphic buffer layers (MBLs) with intentionally mismatched interfaces may be used to take advantage of the strain compensation mechanism.

Previously, we developed a generalized energy minimization model, which determines the equilibrium configuration of an arbitrary compositionally-graded or multilayered heterostructure. The present work focuses on the development of a *novel electrical circuit* model for understanding equilibrium lattice relaxation in InGaAs/GaAs (001) strained-layer-superlattice heterostructures. This work focuses on the design of the SLS buffer layer of In$_x$Ga$_{1-x}$As deposited on a GaAs (001) substrate. The SL contains a set of 10 uniform layers with alternating mismatch. In other words, the SSL contains alternating uniform layers of In$_x$Ga$_{1-x}$As with indium compositions x and x + Δx respectively. For each structure, we present minimum energy calculations and show that for a given SLS total layer thickness h$_{SLS}$, it is possible to find the combination x and Δx such that it provides tight control of the in-plane strain of the strained-layer-superlattice. In addition, for each structure type we present minimum energy calculations by studying the (i) depth profile of strain and (ii) the misfit dislocation density profile. Most importantly, the use of the electrical circuit model allows the analysis of semiconductor heterostructures using a standard SPICE circuit simulator and provides an intuitive understanding of the relaxation process in these multilayered heterostructures.

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

Tribology Focus Topic
Room 101A - Session TR+AS+NS+SS-WeA

Nanoscale Wear: Applications to Nanometrology and Manufacturing

Moderators: Tevis Jacobs, University of Pittsburgh, Filippo Mangolini, University of Leeds, UK

2:20pm **TR+AS+NS+SS-WeA1 A Multi-Bond Model of Single-Asperity Wear at the Nano-Scale***, Y. Shao,* Johns Hopkins University*; T.D.B. Jacobs,* University of Pittsburgh*; **Michael L. Falk**,* Johns Hopkins University **INVITED**

Single-asperity wear experiments and simulations have identified different regimes of wear including Eyring- and Archard- like behaviors. A multi-bond dynamics model based on Filippov *et al.* [Phys. Rev. Lett. **92**, 135503 (2004)] captures both qualitatively distinct regimes of single-asperity wear under a unifying theoretical framework. In this model, the interfacial bond formation, wear-less rupture and transfer of atoms are governed by three competing thermally activated processes. The Eyring regime holds under the conditions of low load and low adhesive forces; few bonds form between the asperity and the surface and wear is a rare and rate-dependent event. As the normal stress increases the Eyring-like behavior of wear rate tends to break down. A nearly rate-independent regime holds under high load or high adhesive forces; bonds form readily and the resulting wear is limited by the sliding distance. In a restricted regime of normal load and sliding velocity, the dependence of wear rate on normal load is nearly linear and independent of sliding velocity, as described by the Archard equation. Detailed comparisons to experimental and molecular dynamics simulation investigations have illustrated both Eyring and Archard regimes and an intermediate cross-over between the two.

3:00pm **TR+AS+NS+SS-WeA3 Surface Chemical and Tribological Studies of Solid Lubricants for Space***, **Jeffrey Lince**,* The Aerospace Corporation **INVITED**

Successful operation of satellites and launch vehicles requires using multiple moving mechanical assemblies (MMAs). The correct choice of lubricants and tribocoatings is critical for the operation of spacecraft MMAs. However, the space environment is challenging. Examples include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. As such, they must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. Although unique synthetic liquid lubricants are used heavily in spacecraft for a variety of applications, solid lubricants are used with many devices because of their low vapor pressure, lack of migration, relative insensitivity to temperature changes, and low contamination potential. Soft solid lubricants such as molybdenum disulfide (MoS_2) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. In addition, increasing interest in low friction nanoparticles has highlighted their potential utility. Tribomaterials show performance in vacuum that differs from that in air. This issue is important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. In addition, degradation during long-term storage can occur, and real-time storage studies correlating surface chemical changes with tribological performance are lacking. In this talk, results will be presented from studies done at The Aerospace Corporation that elucidate the effects of vacuum and temperature extremes on the tribological performance of important spacecraft tribomaterials. Emphasis will be on correlating surface chemical and tribological properties.

4:20pm **TR+AS+NS+SS-WeA7 Molecular Control of Friction***, **Roland Bennewitz**,* INM - Leibniz Institute for New Materials, Germany*; J. Blass, BL. Bozna,* INM - Leibniz Institute for New Materials*; M. Albrecht, G. Wenz,* Saarland University **INVITED**

Molecular films on surfaces can be used to control friction if it is dominated by adhesive shear rather than surface deformation. The underlying molecular mechanisms can be explored by high-resolution friction force microscopy.

We have developed a molecular toolkit for the control of friction and adhesion by supramolecular interactions in aqueous environments. The contacting surfaces are functionalized by cyclodextrin molecules. The interaction is mediated by ditopic connector molecules with hydrophobic end groups which form inclusion complexes with the cyclodextrin molecules on opposing surfaces. Significant friction and adhesion has been measured in atomic force microscopy experiments for connector molecules with adamantane, ferrocene, and azobenzene end groups.

For adamantane connector molecules, adhesion is found to be strongly dependent on the pulling rate due to a transition from subsequent peeling of individual bonds for slow pulling to multivalency effects at fast pulling. In contrast, friction does not depend on the sliding velocity [1].

The use of azobenzene connector molecules allows for switching of adhesion and friction by light stimuli [2]. Switching of friction by electrochemical stimuli for ferrocene connector molecules is less effective due to molecular interactions which are specific to the connector molecules but do not change with the potential [3]. We will discuss differences in rupture and rebinding dynamics for the three connector molecules and their influence on the rate dependence of adhesion and friction.

Cyclodextrin molecules have also been included in stiff polymers whose end groups are attached to tips or surfaces. The polymer-functionalized surfaces exhibit interesting variations of shearing and peeling mechanisms.

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5:00pm **TR+AS+NS+SS-WeA9 Plasticity Controlled Friction and Wear in Single-Asperity Contacts***, **Izabela Szlufarska**, L. Zhao, A. Li, C. Tangpatjaroen, D. Grierson,* University of Wisconsin - Madison **INVITED**

One of the critical challenges in designing materials with superior tribological properties is the current lack of understanding of the microstructural evolution that takes place in sliding contacts. Phenomena that contribute to such evolution are grain growth and refinement, evolution of dislocation networks, and interaction of dislocations with interfaces. In this talk I will discuss examples of how we use multi-scale simulations and atomic force microscopy (AFM) experiments to determine the role of microstructural evolution and plastic deformation in friction and wear. Specifically I will discuss: (i) Our developments of a continuum model that couples grain growth, plastic deformation, and mechanics. This model combines for the first time the phase field method, crystal plasticity, and finite element analysis of mechanical contacts, and parameters for this model are determined from atomistic simulations and experiments. The new model is capable of simulating deformation at strain rates comparable to those encountered in AFM experiments. (ii) Results from our molecular-level simulations on the effects of dopants on strength and wear resistance of nanostructured metal alloys. (iii) Discovery from our complementary AFM and nanoindentation experiments that, although a harder material (silicon carbide) is typically more wear resistant than a softer material (silicon), this trend can be reversed with smaller contact sizes. The contact pressure is the same in both sets of experiments, and both are carried out in the regime where a plastic zone is well-developed. We demonstrate that this surprising finding is due to a transition from abrasive to adhesive wear, which for the first time is observed in single-asperity contacts. Our results show that surface chemistry can have a significant effect on sub-surface plastic deformation.

5:40pm **TR+AS+NS+SS-WeA11 Applying Analytical Roughness Models to Real Surfaces: Reconstructing the Power Spectral Density from Surface Topography Measurements***, **Tevis Jacobs**, A. Gujrati, S.R. Khanal,* University of Pittsburgh*; T. Junge, L. Pastewka,* Karlsruhe Institute of Technology (KIT), Germany

Surface topography is a critical factor for optical, mechanical, and tribological properties of materials. Many studies report single scalar roughness parameters that contain information over just a limited range of wavelengths. Analytical models of roughness have shown in recent years that properties such as stiffness, adhesion, and friction depend on the nature of roughness across many length scales. The power spectral density (PSD) is the mathematical instrument that provides a description of surface roughness as a function of scale. A truly quantitative analysis of surface roughness in terms of the PSD is necessary to validate and apply these analytical roughness models. However, this is currently limited by: (A) inconsistencies in the way that the quantitative PSD is computed; (B) bandwidth-limits of conventional surface metrology; and (C) instrumental artifacts at the smallest scales. Here, we demonstrate these limitations – first, by comparing the various forms of the PSD, then by computing the PSDs both for simulated and experimental surfaces.

We show that experimentally-determined PSDs suffer three types of systematic error, each of which will hinder quantitative comparison to models. We demonstrate strategies for detection and mitigation of these artifacts, to ensure accurate and reliable PSDs. A novel web-based application has been created and made available for general use which computes accurate PSDs and assesses the limits of their reliability. This enables the application of analytical roughness models to calculate upper and lower bounds of surface properties.

Finally, we report on the roughness characterization of an ultrananocrystalline diamond (UNCD) surface over the range from Angstroms to centimeters. This range of characterization enables quantitative comparison with rough-surface adhesion models. By elucidating experimental barriers to accurate surface characterization, and by demonstrating solutions to these barriers, this work facilitates the application of analytical roughness models to real-world surfaces – both to predict and tailor surface properties.

6:00pm **TR+AS+NS+SS-WeA12 Universal Ageing Mechanism for Static and Sliding Friction of Metallic Nanoparticles***, M. Feldmann,* ***Dirk Dietzel****, A. Schirmeisen,* Institute of Applied Physics, Justus-Liebig-University Giessen, Germany

On the macroscale, the distinct difference between static and sliding friction can well be explained by the phenomenon of contact ageing, which is typically related to an increase of contact area with time within a multi asperity interface model. On the nanoscale, however, the role of contact ageing is less clear, especially when considering nanoscale asperities of constant size.

Recently, the role of contact ageing for nanoscale friction dynamics was analyzed for antimony nanoparticles sliding on HOPG. The antimony nanoparticles have been prepared by thermal evaporation on HOPG and comprise an ideal model system with atomically flat interfaces of constant size where friction can be described by the concept of structural superlubricity [1]. Friction of the particles was assessed by nanomanipulation techniques and it was found, that sliding friction can be described as a complex process of thermally activated contact ageing and bond breaking [2]. Further measurements have now revealed, that the particle movement follows an irregular stick slip pattern, where the slip events can be considered as recurring contact renewal, while the stick times can be interpreted as the age of the contact. By correlating the stick times with the lateral force values measured for contact breaking, we found that our system can well be described by logarithmic ageing [3], as it might be expected by assuming atom by atom relaxation processes at the interface.

To check whether ageing during sliding motion is fundamentally different from ageing under stationary conditions, we have performed additional “slide hold slide” measurements [4] and found that in both cases ageing can be described by exactly the same logarithmic function. This indicates, that the strength of the contact is determined by the ageing time but independent of the kinetic conditions. This means that static and sliding friction can be described by a universal ageing law where the age of the contact is the crucial parameter.

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Actinides and Rare Earths Focus Topic
Room 103C - Session AC+AS+SA-ThM

Chemistry and Physics of the Actinides and Rare Earths

Moderators: David Shuh, Lawrence Berkeley National Laboratory, Art Nelson, Lawrence Livermore National Laboratory

8:00am **AC+AS+SA-ThM1 Covalency in Oxidized Uranium***, **James G. Tobin**,* University of Wisconsin-Oshkosh **INVITED**

Actinides, the 5*f* elements and their compounds, alloys, and mixtures, are a crucially important part of modern technological societies. Moreover, uranium dioxide is the most widely used nuclear fuel for the generation of electricity. Yet, because of the complexity of the 5*f*/6*d* electronic structure in the actinides, a fundamental understanding of their physical behavior, in actinides in general and uranium dioxide in particular, has not been achieved.

Theoretically, it has been proposed that covalency is an important part of the electronic structure of actinide dioxide, although some disagree. Experimentally, spectroscopic studies have been reported which support the hypothesis of 5*f* covalency. However, a crucially important and absolutely essential component has been missing: a systematic study where the nature of the oxidant is changed, so the specifics of the 5*f* and 6*d* covalencies could be varied and monitored. The turning-on and turning-off of an effect is the essence of a true benchmarking. The work reported here clearly and irrevocably establishes experimentally the strong presence of U 5*f* –O 2*p* covalency in the unoccupied density of states of UO2, the most important of our nuclear fuels.

This comparative study will feature the isoelectronic systems uranium dioxide (UO2) and uranium tetrafluoride (UF4). While isoelectronic, both being U^{+4} $5f^{\,2}$ in the formal limit, they exhibit substantially different structures. UO2 is a fluorite (cubic) material, while UF4 is monoclinic. However, both exhibit very similar U *L*3 extended x-ray absorption fine structure (EXAFS) behavior, indicative of quantitatively similar interatomic distances. The result of this comparative study is that UF4 exhibits continued 6*d* covalency but the almost complete loss of 5*f* covalency, while UO2 clearly displays both strong 5*f* and 6*d* covalencies. Here we have direct experimental demonstration that 5*f* covalency is important in actinide oxides but can be lost with a more powerful oxidizing agent such as fluorine.

To summarize: Using x-ray emission spectroscopy and absorption spectroscopy, it has been possible to directly access the states in the unoccupied conduction bands that are involved with 5*f* and 6*d* covalency in oxidized uranium. By varying the oxidizing agent, the degree of 5*f* covalency can be manipulated and monitored, clearly and irrevocably establishing the importance of 5*f* covalency in the electronic structure of the key nuclear fuel, uranium dioxide.

Collaborators on this work include: S.-W. Yu, R. Qiao, W. L. Yang, C. H. Booth, D. K. Shuh, A. M. Duffin, D. Sokaras, D. Nordlund, and T.-C. Weng. [*See PHYSICAL REVIEW B **92**, 045130 (2015)]

8:40am **AC+AS+SA-ThM3 An In Situ X-ray Diffraction Study of Plutonium Oxidation***, **Paul Roussel**, W. Lake,* AWE, UK

X-ray diffraction was used to follow the oxidation of α-phase plutonium in oxygen at a pressure of 500 mbar. The composition of the growing oxide scale consisted of the trivalent cubic sesquioxide α-Pu_2O_3 and tetravalent fluorite dioxide PuO_2. The hexagonal β-sesquioxide phase was not detected. The quantity and lattice parameters of the oxide phases were determined from Rietveld analysis of the diffraction patterns. The lattice parameters of both oxides were found to decrease with increasing oxide quantity. Decreasing lattice parameters occur from increasing oxygen anion concentration in each oxide phase. The rate of oxidation for the total oxide composition at various temperatures below 100 °C was found to be linear, indicative of possible moisture enhanced oxidation. A detailed analysis of the contributions of the individual oxide compositions will be presented. Post oxidation optical microscopy of the coherent oxide scale showed areas of thicker scale typical of island growth. When the oxidation reaction was allowed to proceed to form olive green spalled oxide, X-ray diffraction analysis of the powder showed it to consist as a mixture of both cubic oxide phases.

Our initial XRD work presented at this meeting in 2012 suggested the initial oxide film grown on δ-plutonium might be amorphous. This work has been repeated using the XRD in-situ environmental reaction cell and the results will be presented.

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9:00am **AC+AS+SA-ThM4 Advanced Applications of Synchrotron Sources to Describe Water Soluble Plutonium Colloids***, **Thomas Dumas**,* CEA, France*; E. Dalodière, M. Virot,* ICSM Marcoule*; V. Morosini,* CEA Marcoule*; T. Chave,* ICSM Marcoule*; C. Hennig,* Helmholtz Zentrum Dresden-Rossendorf*; T. Wiss,* European Commission, Joint Research Centre (JRC), Institute for Transuranium Elements*; D.K. Shuh, T. Tyliszcaak,* Lawrence Berkeley National Laboratory*; P. Moisy,* CEA Marcoule*; I. Nikitenko,* ICSM Marcoule

Colloidal species of Pu(IV) were shown to play a central role in the speciation of plutonium in various aqueous wastes and in biosphere [1-3]. However, a comprehensive understanding of the behavior and structure of Pu colloids remains elusive and hinders progress on the development of reliable processes of their management. Preparation of plutonium colloidal species with controlled composition and properties is still a challenge. Herein, we report the preparation of stable Pu(IV) colloids by the action of ultrasonic waves on PuO_2 in salt-free water conditions. Sonochemical colloid was compared with hydrolytic colloid using HRTEM, Pu LIII-edge EXFAS and STXM/NEXAFS techniques.

HRTEM revealed nanostructured morphology for both colloids composed of particles of PuO_2 (*fcc*, space group) measuring about 7 nm and 3 nm, respectively. The EXAFS spectra of colloidal PuO_2 nanoparticles were fitted on the basis of PuO_2 cristal structure. Combined HRTEM and EXAFS results revealed the correlation between the coordination numbers (i.e. Pu-O and Pu-Pu) and atomic surface-to-volume ratio of studied PuO_2 nanoparticles.

The STXM/NEXAFS technics implemented at ALS BL 11-0-2 was used for the first time to study plutonium colloids. It offers a new topographic angle to describe colloids combined to spectroscopic measurements at oxygen K edge. It first revealed that the oxygen state of hydrolytic Pu colloid is influenced by hydrolyzed Pu(IV) species in much more extend than the sonochemical colloids. Moreover the topographic analysis highlight discrepancies in plutonium and oxygen distribution for hydrolytic Pu colloid on the contrary to sonolitic one.

Complementarily to previous studies, this work confirmed that plutonium colloids (hydrolytic and sonochemical) can be described as core-shell nanoparticles composed of quasi stoichiometric PuO_2 core and hydrolyzed Pu(IV) moieties at the surface shell. Nevertheless, the application of soft X-ray technics highlight the strong influence of the synthetic route on colloid chemical composition and hence its expectable reactivity.

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9:20am **AC+AS+SA-ThM5 *In Pristinum* Observation of Plutonium Hydride***, **Martin Brierley**, J.P. Knowles,* AWE

The reaction of plutonium with hydrogen creates plutonium hydride in an energetic process which often liberates the reaction product as a powder. Plutonium hydride is pyrophoric; therefore study of the reaction product usually requires that it is passivated by careful exposure to oxygen prior to removal from the reaction chamber. The passivation process is highly energetic with the potential to significantly affect the microstructure of the reaction product and surrounding metal. In this study we used a scanning electron microscope with an adjoining reaction chamber to maintain vacuum between reaction and analysis to grow plutonium hydride and subsequently analyse the reaction products as formed.

Initial work on electro refined Pu gave a slow reaction to hydrogen, requiring an *in situ* heat treatment to form hydride. Analysis of the reaction product was made *in vacuo* following reaction, preventing oxygen from accessing the sample. Subsequent cross sectional analysis of the reaction product morphology was performed, showing a coating of a hydride product layer with an open structure under the original surface oxide [1].

A sample of mixed α/δ phases was successively exposed to hydrogen for increasing durations of 60, 7200 and 70320 s. No evidence of reaction was evident following the 60 s and 7200 s exposures, unlike that observed in experiments on gadolinium [2] and uranium [3]. Following the 70320 s exposure, 96 % of the available hydrogen was consumed and several large anisotropic reaction sites had formed. The hydride sites on this mixed phase sample exhibited anisotropic growth similar to δ-stabilised plutonium samples investigated previously [4]. Deformation of the δ-phases surrounding hydride sites occurred via slip processes. Cracks formed in the overlying oxide layer above the deformed material allowing facile access for hydrogen to reach fresh Pu at the metal/oxide interface. Subsequent cross sectional analysis revealed anisotropic growth of hydride reaction sites, strongly supporting our previously proposed mechanism for anisotropic growth [4]. The α-phase domains resisted deformation and instead transferred the stresses from the hydride reaction front further into the surrounding metal. Post experimental cross sections through reaction sites suggest that hydride regions associated with α-domains had not undergone complete reaction.

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9:40am **AC+AS+SA-ThM6 Evidence for f- and d-orbital Mixing in Lanthanide and Actinide Dialuminides, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, Pu)**, ***Stefan Minasian***, Lawrence Berkeley National Laboratory (LBNL); *A.B. Altman, J. Arnold,* University of California at Berkeley; *E.D. Bauer,* Los Alamos National Laboratory; *C.H. Booth, J.I. Pacold, C.D. Pemmaraju, D.G. Prendergast, D.K. Shuh, T. Tyliszczak,* Lawrence Berkeley National Laboratory (LBNL)

For most scientific and technical applications, aluminum is well-regarded as a trivalent, electropositive and Lewis-acidic metal. However, this textbook model fails to adequately explain the unusual chemical and physical properties of many f-element molecules, materials, and alloys incorporating aluminum and other group 13 elements. In order to develop a more nuanced model of aluminum electronic structure, we have turned to metal K-edge X-ray Absorption Spectroscopy (XAS), which is an established technique for evaluating electronic structure in bioinorganic and inorganic compounds. Pre-edge peaks in K-edge XAS correspond to bound state transitions between core and unoccupied orbitals. Therefore, by comparing pre-edge features to established references, information can be gathered on the electronic structure of a system and the orbitals involved in bonding. However, there is very little precedent for the measurement and interpretation of aluminum K-edge XAS for molecules and materials.

This presentation will describe our recent efforts to develop Al K-edge XAS as a probe of chemical bonding and electronic structure in Al molecules and materials with lanthanide and actinide metals. Work began by examining a series of molecular aluminum compounds and by systematically varying supporting ligands and oxidation states. Features in the Al K-edge spectra were fully assigned through a comprehensive polarization study and comparison with the results of XCH and DFT calculations. Results were interpreted within a molecular orbital framework, providing unique insight that could not be obtained from analysis of NMR or metrics from single-crystal X-ray diffraction. These results have laid a foundation for ongoing efforts with lanthanide and actinide aluminum alloys, MAl_2 (M = Ce, Sm, Eu, Yb, Lu, U, and Pu). Comparisons between the Al K-edge spectra and earlier resonant X-ray emission spectra for the MAl_2 compounds provide unique insight into how electronic structure influences the desirable physical properties of these materials. For $EuAl_2$ and $YbAl_2$, the increasing occupancy of the 4f orbitals enhances screening of the 5d orbitals, resulting in enhanced Al 3p and Ln 5d orbital mixing for Eu and Yb that is not observed for Ce, Sm, or Lu. For UAl_2 and $PuAl_2$, the Al K-edge XAS and theory results also provides convincing evidence of Al 3p and 6d orbital mixing. Because of the enhance radial extension of the 6d orbitals, 6d orbital involvement in bonding for $PuAl_2$ is more likely to have an impact on the stability of the Pu–Al bonds. Current efforts are focused on evaluating f-element interactions with aluminum in other stoichiometric and non-stoichiometric alloys.

11:00am **AC+AS+SA-ThM10 Comparative Analysis of Uranium Oxide Films**, ***Miguel Santiago Cordoba***, Los Alamos National Laboratory

Depleted Uranium (DU) Oxide thin films are considered to be employed as surrogates and reference compounds for systematic studies on the elucidation of fundamental properties of actinide materials. The goal of this work is to compare surface morphologies of DU oxide thin films fabricated by two techniques, polymer assisted deposition (PAD) and electron beam evaporation (EBE). In this contribution, we utilized a MultiMode atomic force microscope (AFM) operating in tapping mode in order to compare and establish a contrast among the three dimensional surface structures of polycrystalline U_3O_8 and UO_2 films fabricated by PAD, and UO_2 thin films deposited by EBE. Differences in surface morphology are analyzed, and the information provided by AFM is compared against other complementary techniques such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Reported results revealed that films fabricated by both techniques had granular structure, with morphologies strongly depending on the fabrication methods and conditions.

*Approved for public release LA-UR-16-22993

11:20am **AC+AS+SA-ThM11 Soft X-ray Spectroscopy of Actinide Materials**, ***David Shuh***, *S.G. Minasian, C. Pemmaraju, A. Canning, D.G. Prendergast,* Lawrence Berkeley National Laboratory; *T. Tyliszczak,* Lawrence Berkeley Lab, University of California, Berkeley; *A. Modin, S. Butorin, J. Nordgren, L. Werme, P. Oppeneer,* Uppsala University, Sweden

Soft X-ray synchrotron radiation methodologies are being developed and employed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory to elucidate the electronic structure of actinide materials. Results from these investigations have begun to provide improved fundamental knowledge that can be used as a scientific basis for the enhanced design of special-purpose actinide materials and the overall understanding of actinide materials. The experimental developments at the ALS have centered on the use of the Molecular Environmental Science (MES) scanning transmission X-ray microscope (STXM) at Beamline 11.0.2 for near-edge X-ray absorption fine structure spectroscopy (NEXAFS), and on X-ray emission spectroscopy (XES) at several beamlines, focusing primarily on light atom constituents (C, N, O, F) for ligand K-edge XAS, and on metal-ion centers plus light-atom signals for XES. The spectromicroscopy capabilities of the STXM provide the means to investigate and determine the speciation in actinide materials and environmentally-relevant systems with spatial resolution that reaches to the true nanoscale. An absolutely critical and key enabling component for all of the soft X-ray investigations is the contribution of theory, that when combined with experiment, has firmly provided more detailed knowledge of electronic structure in actinide materials in terms of orbital composition and mixing, and oxidation state.

Applied Surface Science
Room 101B - Session AS+SS-ThM

Depth Profiling, Buried Interfaces, and 3D Analyses

Moderators: Gregory Fisher, Physical Electronics USA, Karen Gaskell, University of Maryland, College Park

8:00am **AS+SS-ThM1 Pushing the Limits of Bonded Multi-Wafer Stack Heights while Maintaining High Precision Alignment**, ***Alireza Narimannezhad***, *J. Jennings, M.H. Weber, K.G. Lynn,* Washington State University

The last decade in advanced microelectronics has shown great interest in three-dimensional architectures, which was paved by multi-wafer alignment technologies. However, many limitations remain in the fabrication of ultratall stacks as the alignment becomes more challenging and very costly. In this paper, a new cost-effective alignment technique was employed using a set of sapphire rods in through-wafer holes. Cross-sectional analysis, edge profilometry, and electron transmission tests showed ~2 µm alignment tolerances over 1 cm and ~4 µm over 10 cm tall stacks. An off-angle gold sputtering method was developed to fully coat vias of 5:1 aspect before bonding. Also, a new *Stamping* technique is introduced to coat the vias to a desired height where necessary. In this study, parallel microtubes with aspect ratios of 1,000:1 were formed by aligning ~200 wafers, each including 20,000 gold-coated vias for storing charged particles.

8:20am **AS+SS-ThM2 Porous Si Stack Analysis by Model Based Infrared Reflectometry (MBIR)**, ***Sukti Chatterjee***, *L. Scudder, P. Narwankar,* Applied Materials Inc.

In 1956, Porous silicon (PS) was accidentally discovered by Uhlir at Bell Laboratories [1], and t he material was very much ignored. Later (70's and 80's) porous Si was found to be useful because its high surface area [2-5] for various applications, like microcavity, broadband AR coating, mid infrared LEDs, chemical Sensors, smart Dust, pressure Sensor, photonic crystal. Recent interest of porous Si is in the biomedical *field [6] with wide range of applications*, ex. drug delivery, cancer therapy, and tissue engineering. For diverse applications, single or multilayers porous Si stacks are required. In this abstract we present our metrology invention for single or multilayers porous Si stacks analysis.

We introduce a novel approach to characterize the different Si film stacks by using Model Based Infrared Reflectometry (MBIR). We believe, we are first group to apply the technique for analyzing various multilayer Si stacks. The film stack thickness has varied between 1 µm to more than 100 µm. Thick layers of silicon are opaque in the UV-VIS wavelength range, and IR wavelengths are ideal for measurements of such films. The ability to specify a film stack in the MBIR analysis model makes the technique more versatile, compared to traditional FTIR. We will present in the conference how the IR optical properties of PS can be described by Bruggeman Effective Medium Approximation (EMA), employing a standard multilayer reflectance model. To validate the MBIR results x-SEM and Gravimetric analysis have been used. The results have shown MBIR to be a suitable technique for characterization and production monitoring of the process steps associated with the new porous silicon applications field.

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6. Porous Silicon for Biomedical Applications, Edited by: H.A. Santos ISBN: 978-0-85709-711-8

8:40am **AS+SS-ThM3 Applications of Atom Probe Tomography on 3D Semiconductor Devices***, **AjayKumar Kambham**, D. Flatoff, P.A.W. van der Heide,* GLOBALFOUNDRIES U.S. Inc. **INVITED**

One of the aims in CMOS device development is to reduce power consumption while increasing performance. Pivotal to this, is the critical need to engineer dopant profiles, and to define the formation of the appropriate junctions. Tied to this is the increased severity of short channel effects (SCEs) as dimensions are decreased, hence the reason to move to 3D structures in the form of FinFETs. One type of SCE that is known to cause performance degradation is Drain Induced Barrier Lowering (DIBL). To reduce DIBL, dopant junction profiles are made more abrupt. This can be done through the introduction of Sigma/cavity, fully depleted silicon-on-insulator (FDSOI) structures and the modulation of stress through optimal engineered epitaxial buffer layers. To assess the quality of interfaces in these different structures over nanometer scale regions requires the use of analysis techniques such as Atom Probe Tomography (APT) and Transmission Electron Microscopy (TEM). This presentation will discuss the ability of APT to extract the critical information of interest to device engineering.

9:20am **AS+SS-ThM5 Analysis of ALD/CVD Thin Film Conformality using Lateral High Aspect Ratio (LHAR) Structures: Experimental Characteristics and Proposed Classifications***, **Riikka Puurunen**,* VTT Technical Research Centre of Finland*; J. Dendooven, V. Cremers, C. Detavernier,* Ghent University, Belgium

High conformality—the ability of a thin film to cover a complex three-dimensional substrate uniformly—is a key advantage of atomic layer deposition (ALD) compared to chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes. More than 700 ALD processes (with unique reactant pairs/activation) have been reported, as calculated from Ref. [1]. Conformality has been experimentally studied for a small minority of these, most likely because of the lack of easily available test structures and accessible methods of analysis.

When conformality is investigated, most typically, vertical trenches (or holes) etched into silicon, typically with aspect ratio (AR) up to around 50:1, are used and the results are analysed point by point by cross-sectional electron microscopy. Comparison of results obtained in different studies is difficult because of the lack of standard test structures and standard means of analysis, and the large variety of process conditions that are used. The theoretical framework for interpreting the conformality results is also underdeveloped.

To develop the conformality analysis, we have reported on macroscopic [2, 3] and microscopic [4] lateral high aspect ratio (LHAR) test structures. In contrast to vertical HAR, LHAR structures allow one to investigate thin film thickness and properties in very demanding aspect ratios (>10 000:1) and obtain accurate information of film thickness and properties along the feature by standard means of measurement such as ellipsometry and reflectometry. The purpose of the present work is to compare results obtained for different thin film processes in different test structures (our own + literature) using the highly studied [1, 5] Me3Al/H2O ALD process as baseline. We propose a classification scheme for how the thickness line profiles are expected to vary inside LHAR structures in different cases of characteristic governing growth chemistries.

Acknowledgements: This work has been funded by the Finnish Centre of Excellence in Atomic Layer Deposition, BOF-UGent, FWO-Vlaanderen and SIM-Flanders (TRAP-FUNC project). Feng Gao and Meeri Partanen are thanked for fabricating the microscopic LHAR structures.

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9:40am **AS+SS-ThM6 *In Situ* Liquid SIMS Investigation of Chemical Components of the Solid-Electrolyte Interface in Li Ion Batteries***, **Zihua Zhu**, C. Wang, Y. Zhou, D.R. Baer, W. Xu, R. Cao, X. Yu, P. Yan, R. Zhao,* Pacific Northwest National Laboratory

Since the birth of Li-ion battery, Solid-Electrolyte Interface (SEI) has been a hot research topic, and numerous efforts have led to some information about its chemical composition, formation mechanism and degradation process. However, critical questions that can enable the design of advance battery systems remain unanswered because it has been very difficult to molecularly examine the SEI layer during battery operation. For example, in situ TEM has been used to study the formation process of the SEI layer in Li ion batteries; however, mostly morphological information, but very limited chemical information is obtained. In situ liquid SIMS was developed in Pacific Northwest National Laboratory (PNNL) in the last several years, and it has proven a very promising new technique to provide both elemental and molecular information at solid-liquid interfaces. In this work, a model Li-ion battery was designed for in situ liquid SIMS analysis of SEI layer. A ~70 nm thick Cu film was deposited onto a SiN membrane, which served as anode. Cathode was traditional LiCoO$_2$. 1.0M LiPF$_6$ in EC (ethylene carbonate)/DMC (dimethyl carbonate) was used as electrolyte. Li$_2$O and LiOH are found in the SEI layer, while very little LiF is observed, indicating LiF is not an important component in the SEI layer. More interestingly, solvent molecules are found in the SEI layer, and the major component is DMC but not EC. In addition, very little PF$_6^-$ is found in SEI layer. This is the first time that molecular information of the SEI layer is obtained, and the new information will greatly advance understanding formation mechanism and degradation process of SEI layer.

11:00am **AS+SS-ThM10 Electronic and Physical Changes to Soft Materials Caused by Gas Cluster Sputtering***, **Christopher Goodwin**, Z.E. Voras, T.P. Beebe, Jr.,* University of Delaware

The development and application of gas cluster ion sputtering (GCIS) of soft materials opens the ability to perform 3D analysis without removing the sample from a vacuum environment. GCIS has been used to remove material from the surface of some samples without leaving behind a significant amount of damaged material. This allows for depth profiling and sample cleaning in vacuum, without loss of chemical information. The soft sputtering standard Irganox 1010 has been used to study topological effects of GCIS with atomic force microscopy (AFM) while chemical changes were monitored with X-ray Photoelectron Spectroscopy (XPS). In addition to Irganox 1010, polyaniline has been studied due to its importance as an organic conductive material, allowing for many applications such as a solar cells, antistatic and corrosion-resistant coatings, and superconductors. GCIS was used to depth profile into thin films of polyaniline, resulting in some topological (AFM) and chemical changes (XPS). Our interest is in exploring how these changes caused by GCIS sputtering affect the electronic band structure of conductive polymers.

11:20am **AS+SS-ThM11 FIB-TOF Characterization of Organic and Organic/Inorganic Structures**, ***David Carr**, G.L. Fisher, S.R. Bryan,* Physical Electronics*; S. Iida, T. Miyayama,* ULVAC-PHI, Japan

1. Introduction

Probing the sample chemistry beyond the surface region with ion beam sputtering is subject to practical limitations which include preferential sputtering, accumulated sputter beam damage, inclusions, and voids. These effects can result in a distortion or complete loss of the true chemical distribution as a function of depth.

In situ FIB milling and sectioning with TOF-SIMS chemical imaging (3D FIB-TOF tomography [1]) is an alternative approach to achieve 3D chemical imaging of complex matrix chemistries. The FIB milling can minimize or eliminate artifacts caused by sputter depth profiling from the surface.

For matrices with organics components, however, FIB beam-induced chemical or molecular damage may limit the detection of characteristic molecular signals. The characteristic molecular signals can often be recovered with cluster ion polishing to remove the organic FIB damage.

2. Method

The 3D chemical characterization of organic and organic/inorganic mixed composition structures was achieved utilizing FIB-TOF on a PHI TRIFT *nanoTOF* II (Physical Electronics, USA) imaging mass spectrometer equipped with the new parallel imaging MS/MS [2,3]. The spectrometer's large angular acceptance and depth-of-field maintain high mass resolution and high mass scale linearity in this challenging geometry.

3. Results

Results will be presented for structures with mixed organic phases and mixed organic/inorganic phases. The FIB-TOF results will be compared with corresponding sputter depth profiling results to highlight the relative advantages of the two techniques along with potential complicating factors to the analyses. The high sensitivity of the TOF-SIMS technique is not limited to strong organic matrix peaks. Data will be presented showing the ability to probe the 3D distribution of polymer additives in a sample. The identity of the additives is confirmed using the newly developed parallel imaging MS/MS option for the *nanoTOF* II. The ability to study buried organic structures with FIB-TOF and then conclusively identify the detected species using MS/MS is a powerful new development for the field of TOF-SIMS.

4. References

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11:40am **AS+SS-ThM12 Molecular Depth Profiling with a New Hybrid 3D SIMS instrument for Improved Molecular Identification**, ***Alexander Pirkl**, R. Moellers, H.F. Arlinghaus,* ION-TOF GmbH, Germany*; N.J. Havercroft,* ION-TOF USA*; E. Niehuis,* ION-TOF GmbH, Germany*; A.A. Makarov, S. Horning,* Thermo Fisher Scientific*; R. Havelund, M.K. Passarelli, A.G. Shard, I.S. Gilmore,* National Physical Laboratory, UK

Introduction

Depth profiling of organic layers for optical and electronic devices can be ideally performed using gas cluster ion beams (GCIB) in combination with time-of-flight secondary ion mass spectrometry (TOF-SIMS). For optimum performance a dual beam approach is utilized, employing a lower energetic quasi DC sputter beam for material removal and a short pulsed small spot analysis beam for optimal mass spectral and imaging performance.

However molecular identification of unknown substances, e.g. contaminants, is usually hampered by constraints in mass resolution and mass accuracy of the TOF analyser. Furthermore ions generated in the sputter phase of the dual beam experiment are lost for the MS analysis. In order to overcome these limitations a TOF/Orbitrap^{TM}-SIMS hybrid mass analyser instrument was developed.

Methods

A prototype SIMS instrument with a hybrid TOF/Orbitrap mass analyser was utilized for acquisition of organic depth profiles. During sputtering with 5-20 keV argon clusters secondary ions can be detected using the Q Exactive^{TM} HF mass analyser. Selective ion gating was implemented to avoid artefacts from the crater walls. *In situ* tandem MS analyses of the most abundant peaks were used to confirm the mass assignments. Imaging TOF analysis with high lateral resolution was performed on the same instrument using short pulses from a 30-60 keV Bi-liquid metal ion gun (LMIG) and a dedicated TOF.SIMS V analyser for comparative measurements.

Preliminary Data

Molecular depth profiles were acquired using GCIB induced desorption in a single beam approach from organic test structures and organic LED materials. The high mass resolution of 240 000 of the Q Exactive HF mass spectrometer proved to be essential for separation of otherwise overlapping ion signals. Molecular assignments based on the high mass accuracy below 3 ppm were validated using tandem MS analysis. Up to 5 decades of dynamic range and a depth resolution below 8 nm were found to be possible with this approach leading to unprecedented depth profiling results.

Depth profiles and according spectra are compared to the classical dual beam approach. While depth resolution is similar, differences in the relative signal intensities were observed in spectra from the two different ion beams. Implications for the analysis of biological samples will be discussed.

12:00pm **AS+SS-ThM13 3-D Analysis of Binding-Medium Degradation as Related to Renaissance-Era Artwork**, ***Zachary Voras**, C.M. Goodwin,* University of Delaware*; J.L. Mass,* Rijksmuseum*; K.R. DeGhetaldi,* Winterthur Museum*; T.P. Beebe, Jr.,* University of Delaware

In historical art objects, binding-medium degradation involves complex chemistries that can occur at the surface or interface of a paint layer. These can propagate inward toward the bulk material, caused by inherent impurities within the paint that migrate throughout the paint layer. These effects can cause mechanical failure due to binding-medium degradation, primarily observed as paint-layer flaking, spalling, and fracture. Our prior research performed on Renaissance-era artwork has indicated two major correlations to the severity of binding-medium degradation: i) depletion of long-chain fatty acid components within the binding medium of a paint layer, and ii) alteration of the amino-acid composition of proteinaceous materials comprising the binding medium. In this study, the effects of controlled aging factors (i.e., heat, humidity, and UV exposure) on thin films of egg tempera were observed through the use of x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). The newly available technology of gas cluster ionization sources (GCIS) allows for the ability to depth profile through some soft organic and biological materials with no little or no ion-induced damage. By using an argon-cluster ion beam to depth profile through a degraded thin film, a 3-dimensional analysis of short- and long-range degradation effects, followed by XPS and ToF-SIMS, respectively, was performed. Since ultramicrotomy is an established sample-preparation technique in the art conservation field, results of GCIS will be compared to ultramicrotomy as sample preparation method for organic and biological thin films.

Biomaterial Interfaces
Room 101A - Session BI+AS+SA-ThM

Synthesis and Processing of Biomaterials/Biologically Inspired Materials

Moderators: Daniel Barlow, US Naval Research Laboratory, Lara Gamble, University of Washington

8:00am **BI+AS+SA-ThM1 Response of PC 12 Cells to Mesoporous Substrates with and without DC Bias**, *F. Sabri,* University of Memphis*; **Kyle Lynch**,* Universtiy of Memphis*; O. Skalli,* University of Memphis

The interaction of nerve cells with nanostructured surfaces and substrates is of great importance to the field of tissue engineering and artificial substrates developed for biomedical applications. It has been established that cells respond to different polymer surface characteristics such as roughness, surface free energy, topography, chemistry, charge, and other properties including electrical conductivity. It has also been recognized that the nanotopography can affect and influence cell morphology, cell alignment, cell signaling and extension of neurites. Here, we discuss the influence of the mesoporous structure of crosslinked silica aerogels on the adhesion, proliferation, and neurite extension of PC 12 cells, in the presence and absence of applied DC bias. The behavior of cultured PC 12cells on the aerogel substrates is compared to the behavior of cells cultured on cell culture plastic (control) and the affect of applied DC bias of different magnitudes is carefully investigated. The neurite extensions clearly show a preferred growth direction and the rate of growth of extensions is also influenced by the varying conditions.

8:20am **BI+AS+SA-ThM2 Collagen Functionalized with ALD-TiO_2: A Novel Biomaterial for Bone Grafting***, **ArghyaKamal Bishal**, C. Sukotjo, C.G. Takoudis,* University of Illinois at Chicago

In medicine, the use of implants is growing rapidly. Some patients may not have enough bone to support such implants.[1, 2] Therefore, those patients are required to have augmentation, a procedure to increase the height or width of inserted bone-like supporting materials, prior to implantation.[1] Collagen resorbable membrane is used as a bone grafting material which acts as supporting material and facilitates new bone formation.[3] Sometimes, titanium reinforced collagen membrane is used for improved stability.[2]

Collagen is an important biomaterial which is used in several biomedical applications. It has a triple helix structure made of polypeptide chains.[3, 4] Hydrogen bonds play an important role in keeping together these peptide chains. Glycine, proline are the most abundant amino acids found in its structure. Collagen has also the ability to be reorganized and crosslinked and thus turn into flexible fibrils with higher tensile strength.[3]There are four main types of collagen: type I, II, III and V. Among them mostly type I and little amount of type V construct the bone structure by forming a composite with hydroxyapatite (HA) crystals.[4]

Titania (TiO_2) itself is biocompatible.[5] Additionally, it has the ability to attract Calcium and Phosphate in a liquid environment.[6] Therefore TiO_2 coated collagen may be used as an excellent bone grafting material to nucleate Ca and P and thus reconstructing a stable bone structure. In this work, we present ALD of TiO_2 on collagen membrane in a custom-made ALD reactor. The deposition was performed at room temperature. Tetrakis(dimethylamido)titanium (TDMAT) and ozone were used as metal precursor and oxidizer, respectively. Samples were characterized for their surface morphology, composition and mechanical properties. Energy dispersive spectroscopy confirmed the presence of Ti on coated collagen and electron microscopy showed an increase in fiber diameter after deposition by more than a factor of 2:

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8:40am **BI+AS+SA-ThM3 Nanostructure Formation on Biomaterials by Directed Irradiation Synthesis (DIS) for Tissue Regeneration and Maximize Corrosion Resistance***, **Jean Paul Allain**, A.R. Shetty,* University of Illinois at Urbana-Champaign*; S. Arias, A. Barnwell,* University of Illinois at Urbana Champaign*; F. Echeverria, L.F. Berrio,* University of Antioquia, Colombia

An important aspect of tissue engineering is to create a favorable extracellular microenvironment, mainly the extracellular matrix (ECM) which can guide cell differentiation and tissue regeneration. The ECM consists of a number of cues that can be guided by surface topography and matrix stiffness [1]. Recent studies [2,3] have demonstrated that depending on the type of surface structuring and patterning, cell adhesion can be controlled with potential applications in smart cell culture systems and biosensors. Many of the desired biomaterial properties that require a combination of metal alloy and soft material interfaces cannot be processed with conventional bottom-up techniques. Directed irradiation synthesis (DIS) address this limitation by introducing a synthesis process that is scalable to high-volume manufacturing by virtue of its intrinsic large-area simultaneous exposure of materials surfaces and interfaces.

In this study, we have employed directed irradiation synthesis to induce nanostructure formation on two commonly used biomaterials: 1) Ti_6Al_4V and 2) magnesium (Mg). The goal is to examine the role of surface nanostructuring on the stimulation of cells and tissues in order to provide important cues for tissue regeneration as well as guarantee a good corrosion resistance and to minimize bacteria adhesion. Detailed characterization, establishing processing conditions and correlating them to surface and biomaterial properties have been successfully performed on nanostructured medical grade Ti_6Al_4V and Mg. These irradiated surfaces were biologically evaluated by using human aortic smooth muscle cells (HASMCs) for cytotoxicity and cell/surface adhesion and interactions. This analysis allowed us to determine connections with processing, structure, surface energy, and biointerface properties. Biological response of these new surfaces has also lead us, for the first time, to establish correlations between nanostructuring by DIS and cell stimulation, as well as to show the real potential of these new surfaces to favorably stimulate cells and tissues different than bone. The corrosion behavior of these biomaterials in a phosphate buffered simulated body fluid (SBF) has also been investigated for bone implant application.

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9:00am **BI+AS+SA-ThM4 Controlled Peptide Surfaces of Various Ratios that Guide Neural Stem Cell Differentiation***, **HalaShakib Dhowre**, M. Zelzer, H. Sahaf, C. Towlson, N.A. Russell,* University of Nottingham, UK

Cell instructive biointerfaces represent an essential aspect for the advancement of regenerative medicine. Currently, a major issue in biointerface design is the limited ability to mimic the complex interactions of the natural processes in the extracellular matrix (ECM) with artificially designed surfaces and interfaces [1]. While biomaterial surfaces have been shown to be able to elicit specific cell responses (e.g. adhesion, proliferation, differentiation), precise control akin to that of natural cellular environments is still lacking[2].

AIM:

The present work aims to address this challenge by designing new synthetic peptide surfaces with well controlled composition and functionality able to impact control over the differentiation of neuronal stem cells with the ultimate goal to understand and control how neuronal networks function.

METHODS:

Compositionally well defined surface concentrations of two short laminin peptide sequences, Arg-Gly-Asp (RGD) and Ile-Lys-Val-Ala-Val (IKVAV) were prepared of various ratios via the “grafting from” stepwise approach and the surface modification was confirmed with surface analysis techniques to indicate successful peptide functionalisation. The neural stem and progenitor cells (NSPC) were set up from embryonic rat hippocampi (E18). Immunocytochemistry (ICC) observed cell viability and differentiation to specific NSPC lineages for Nestin, βIII-Tubulin and GFAP.

RESULTS:

Surface characterising techniques (WCA, AFM and ToF-SIMS) verified the successful amino acid build-up to peptides on the surfaces, allowing modification of the surfaces with RGD and IKVAV. Enhanced NSPC adhesion, proliferation and differentiation were observed on the peptide surfaces. ICC demonstrated Nestin expression decrease after the removal of the growth factors (EGF and FGF) and an increase in the expression of βIII-Tubulin and GFAP; thus illustrating cells differentiating from stem cells to neurons or astrocytes due to peptide surface influence.

CONCLUSION:

Well defined peptide surfaces were designed successfully, the various ratios of RGD and IKVAV surfaces demonstrated cell adhesion, proliferation and i desirable effects in controlling different populations of stem cell fate. These surfaces may advance new insight in understanding how surface properties affect the regulation of physiological relevance in directing neural cell differentiation, which will be essential to understand how neural networks function.

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9:20am **BI+AS+SA-ThM5 Biofunctional Hydrogels for Tissue Repair*, Andres Garcia,*** Georgia Institute of Technology **INVITED**

Hydrogels, highly hydrated cross-linked polymer networks, have emerged as powerful synthetic analogs of extracellular matrices for basic cell studies as well as promising biomaterials for regenerative medicine applications. A critical advantage of these synthetic matrices over natural networks is that bioactive functionalities, such as cell adhesive sequences and growth factors, can be incorporated in precise densities while the substrate mechanical properties are independently controlled. We have engineered poly(ethylene glycol) [PEG]-maleimide hydrogels to study epithelial morphogenesis and identified independent contributions of biophysical and biochemical properties of these materials to this developmental process. In another application, we have developed synthetic hydrogels that support improved pancreatic islet engraftment, vascularization and function in diabetic models. These studies establish these biofunctional hydrogels as promising platforms for basic science studies and biomaterial carriers for cell delivery, engraftment and enhanced tissue repair.

11:00am **BI+AS+SA-ThM10 Nanoscale Domain Formation Induced by Partial Polymerization Creates Planar Supported Lipid Bilayers that are Fluid and Stable*, N.Malithi Fonseka*,** *B. Liang, K.S. Orosz, C.A. Aspinwall, S.S. Saavedra,* University of Arizona

Planar supported lipid bilayers (PSLBs) are widely explored bilayer platforms for receptor-based biosensors. PSLBs composed of fluid lipids lack the stability necessary for many technological applications due to the relatively weak non-covalent interactions between lipid molecules. Lipid polymerization enhances bilayer stability, but may greatly reduces lipid mobility and membrane fluidity. In an effort to enhance bilayer stability while maintaining fluidity, we have prepared and characterized PSLBs composed of mixtures of the polymerizable lipid bis-Sorbyl phosphatidylcholine (bis-SorbPC), and the fluid lipid diphytanoyl phosphatidylcholine (DPhPC) to form mixed PSLBs. We measured lateral diffusion coefficients (*D*) as a function of the bis-SorbPC/DPhPC molar ratio using fluorescence recovery after photobleaching (FRAP). In pure DPhPC PSLBs, *D* = 0.66 µm^2/sec. In equimolar poly(bis-SorbPC)/DPhPC, *D* = 0.36 µm^2/sec, whereas when the ratio is greater than 0.7, *D* decreased to 0.13 µm^2/sec. These data show that considerable fluidity is retained even when the poly(bis-SorbPC) fraction is substantial, which suggests that these bilayers are phase segregated, composed of polymerized and fluid domains. However domains were not observed with fluorescence microscopy techniques. The sub-µm morphology of these PSLBs was therefore investigated using atomic force microscopy (AFM). Nano-scale phase segregation of the two lipids was observed. DPhPC forms a continuous lipid matrix that is 0.2-0.4 nm thicker than the island-like poly(bis-SorbPC) domains. This height difference agrees with bilayer thicknesses measured for pure DPhPC and poly(bis-SorbPC) PSLBs. Furthermore, it was observed that the size of the poly(bis-SorbPC) domains increased with the percentage of poly(bis-SorbPC) in the PSLB. In summary, mixed lipid bilayers composed of poly(bis-SorbPC) and DPhPC form nano-structured membranes with retained lipid diffusivity, and thus they have considerable potential for creating membrane-based biosensors in which receptor activity depends on bilayer fluidity.

11:20am **BI+AS+SA-ThM11 Stabilization of Lipid Films by Hyaluronic Acid and Polymeric Substitutes in a Joint Model System*, Felicitas Schwoerer,*** Universität Heidelberg, Germany*; M. Trapp, R. Steitz,* Helmholtz-Zentrum Berlin für Materialien und Energie GmbH*; R. Dahint,* Universität Heidelberg

In the United States there are 27 million people suffering from osteoarthritis. The disease is primarily caused by the degeneration of cartilage, which covers the bone ends of the joints and is in turn decorated with a phospholipid (PL) layer. The bone ends are separated by the synovial fluid containing the polysaccharide hyaluronic acid (HA) as a main component. It is generally assumed that both HA and PLs reduce friction and protect the cartilage. Based on the observation that HA concentration is reduced in diseased joints, a new cure called viscosupplementation has been developed, where HA or mixtures of HA and PLs are injected into the joints. However, until now the positive effect of such therapy is under debate.

To elucidate the importance of HA and PLs for joint lubrication and protection on a molecular level we investigate their interaction using a simplified model system for natural joints. A silicon wafer (representing the bone end) is covered with PL oligobilayers and incubated in an aqueous solution containing HA or polymeric substitutes (representing the synovial fluid). To mimic the forces in joint movement, we expose the model surfaces to a home-built shear apparatus facilitating *in situ* measurements at a rotational speed between 0 rpm and 6000 rpm. Measurements were performed at *BioRef* (Helmholtz-Zentrum Berlin), a time-of-flight neutron reflectometer with integrated infrared spectroscopy.

Upon contact with both HA and poly(allylamine hydrochloride) (PAH) solutions a tremendous swelling of the lipid film occurs. Film thickness increases by a factor of about four compared to pure D_2O exposure due to a drastic increase in the thickness of the interstitial water layers located between adjacent lipid bilayers. This effect is most likely due to the adsorption of charged polymers at the lipid headgroups leading to electrostatic repulsion. Despite their high film thickness and water content, the polymer-exposed lipid films exhibit approximately ten times higher shear stability than the respective systems incubated in pure water. With increasing rotational speed the lipid films contain substantially enhanced water fractions, which we attribute to increasing lateral fragmentation. Present investigations aim at the question whether HA and PAH are incorporated into the lipid tail region and bridge adjacent bilayers as this might explain the observed higher stability.

11:40am **BI+AS+SA-ThM12 New Substrates and Patterning Methods for Supported Lipid Bilayers*, Sally McArthur*,** *L. Askew,* Swinburne University of Technology, Australia **INVITED**

The cell membrane encases and protects cellular components and plays an important role in transport, signalling and disease. Studying membrane behaviour is a challenging task due to the complexity and scale on which these processes occur. Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. The planar structure of the model means a variety of patterning techniques can be employed to recreate membrane architecture on both a micro and nanoscale. In particular, pre-patterned substrates are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymers provide a versatile method of creating thin films with a variety of different surface chemistries. In this work we explore the behaviour of plasma coatings in aqueous conditions and the use of plasma films for creating patterned SLBs using vesicle collapse. The results demonstrate that variations in plasma polymer chemistry can be used to control lipid bilayer formation and the locations of different lipid species. Characterisation of film behaviour and bilayer formation was conducted using a variety of techniques including ellipsometry, quartz crystal microbalance with dissipation (QCM-D), confocal microscopy, atomic force microscopy (AFM) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS).

Applied Surface Science
Room 101B - Session AS-ThA

Advances for Complicated Sample Preparation Strategies and Complex Systems

Moderators: Christopher R. Anderton, Pacific Northwest National Laboratory, Michaeleen Pacholski, The Dow Chemical Company

2:20pm **AS-ThA1 Measuring Nanoparticle Properties: Are We High and Dry or All at Sea?*, Caterina Minelli,*** National Physical Laboratory (NPL), UK **INVITED**

Reliable and reproducible measurement methods for nanoparticles will significantly impact the uptake of these materials in commercial applications and allow industry to comply with regulation. However, there are significant challenges in the analysis of nanomaterials due to, among other factors, the interdisciplinary nature of the field, the lack of adequate reference materials to calibrate analytical tools and the difficulties associated both with sample preparation for analysis and the interpretation of data. Furthermore, the inconclusive outcomes of nanoparticle toxicity risk assessments can largely be traced to a failure to address these measurement challenges.

The preparation of nanoparticle samples for analysis can significantly alter both the nanoparticles themselves and the results of the analysis. Measuring colloidal nanoparticles using vacuum-based techniques is particularly prone to artefacts and irreproducibility introduced by sample preparation. In order to produce relevant and meaningful data from nanoparticle analysis it is therefore important to establish sound sample preparation protocols. It is good practice to use a combination of techniques which can be employed directly to the colloidal suspension and on the dried particles to ensure a meaningful interpretation. Examples which will be discussed include the measurement of the density of polymeric nanoparticles by small angle X-ray scattering (SAXS) and analytical centrifugation, and the analysis of the protein coatings on gold nanoparticles in liquid media (*in-situ*) and *ex-situ* with high vacuum techniques such as X-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). The challenges in sample preparation for these methods and the difficulties of data interpretation will be described in detail. The *in-situ* measurement of nanomaterials in complex matrices is highly sought after by industry and regulatory bodies, but remains an unmet challenge. The potential application of new methods, such as non-linear optical techniques, will be considered.

Inter-laboratory studies enable the refinement of sample preparation protocols, which in turn have a positive impact on the broader adoption of the analytical method for nanoparticle characterisation. We will discuss the main outcomes of a VAMAS inter-laboratory study whose aims included to assess the inter-laboratory variability in the measurement of nanoparticle coatings using XPS and LEIS and identify sources of variability in sample preparation procedures. This work will directly input into ongoing efforts in ISO TC201 to standardize the surface chemical analysis of nanoparticles.

3:00pm **AS-ThA3 The Secret Life of Nanoparticles: Often Ignored Characteristics of Nano-Objects That Limit Reproducibility and an Approach to Improving Data Collection and Reporting to Address the Challenges*, Donald Baer,*** Pacific Northwest National Laboratory

The literature is filled with images of nanoparticles and nanostructured materials along with descriptions of how they were synthesized and some aspects of their new and exciting properties. However, nano-objects present fundamental synthesis, characterization, and handling challenges that are often ignored or unrecognized by parts of the scientific and technical community. The frequent tendency of such particles to interact with surrounding media and to respond to environmental changes complicates understanding their properties as a function of time in different environments but also presents interesting opportunities for the design of particles with desired time dependent properties. Particle variation due to time and environmentally dependent changes raise a number of issues associated with particle preparation for analysis, especially surface analysis. Issues include knowing the nature of changes and the rate at which they change after synthesis, during storage and processing, and in different media. This presentation will highlight some of the behaviors of nanoparticles we have observed drawing on research on Fe oxide-shell metal-core, ceria, and Ag nanoparticles. Examples will include the impact of particle structure on the dissolution and toxicity of Ag nanoparticles, the environmentally induced changes in the chemical state of ceria nanoparticles and the impact of synthesis details on the ability of iron metal-core oxide-shell particles to reduce contaminants in ground water. Some of the inconsistences in the literature are aggravated by the under-recording and under-reporting details of particle synthesis and handling. An ISO standard being developed to help address the problem will be described. This draft document includes both a standard on reporting of the preparation of particles for surface analysis and information about a range of sample preparation methods optimized for the types of information desired. One focus of the document is in on the extraction of nanoparticles from solution for analysis of surface coatings.

3:20pm **AS-ThA4 Combined XPS/ISS/UPS Study of Ultra-thin HfO_2 films on SiO_2/Si Substrateso*, Paul Mack,*** Thermo Fisher Scientific, UK

Hafnium oxide (HfO_2) films are often found in microelectronic devices, where they are used as gate dielectrics, for example. As device dimensions become smaller and smaller, it becomes necessary to make thinner HfO_2 films, which may only be a few nanometers thick. X-ray Photoelectron Spectroscopy (XPS) is an analysis technique which non-destructively provides chemical bonding information from the top few nanometres of a surface. It is the ideal technique to analyse the hafnium or silicon chemical bonding environment or to measure the thickness of these ultra-thin films. XPS cannot easily measure the coverage of ultra-thin films, however, but the complementary technique of Ion Scattering Spectroscopy (ISS) can be used for this purpose.

There is also a requirement for understanding the electronic structure of ultra-thin HfO_2 films. Ultraviolet Photoelectron Spectroscopy (UPS), using a helium discharge lamp for generate He(I) or He(II) photons (with energies of 21.2eV and 40.8eV, respectively), can be used to measure the work function of conductive films and to investigate valence electronic structure.

This talk will present data from XPS/ISS/UPS studies of a series of ultra-thin HfO_2 film films on SiO_2/Si substrates. The samples were created with varying numbers of ALD cycles, to generate HfO_2 films of different thickness and coverage. The results will demonstrate that using a complementary analytical approach, with all three techniques available on a single tool, provides a much more comprehensive analysis of the HfO_2 films than would be possible with only one analytical technique.

4:00pm **AS-ThA6 A Novel Method for Matrix Application in Matrix Enhanced SIMS Imaging*, Matthias Lorenz,*** *A.G. Shard, J.-L. Vorng, I.S. Gilmore,* National Physical Laboratory, UK

We report on a novel method for controlled and versatile application of matrix compound for the purpose of matrix enhanced secondary ion mass spectrometry (ME SIMS). General applicability of this approach for ion signal enhancement of drug molecules and endogenous compounds in drug dosed tissue homogenate is demonstrated.

A major problem for SIMS imaging in life-sciences is the signal-limited spatial resolution and matrix effects that suppress ion yields. In severe cases, the ion signal may be lost all together. This leads to the adage that not seeing a molecule in SIMS does not mean it is not there. One route forward is to use a molecule to enhance the signal as done in matrix assisted laser desorption/ionization (MALDI). However, it is well-known that this causes redistribution of analytes (such as drugs) over tens of microns. This circumvents the resolution benefit of SIMS over MALDI. Furthermore, methods used for MALDI are not suitable for 3D imaging, where the matrix layer would be sputtered away. We report on a novel technique for the controlled application of matrix compounds specifically for ME SIMS that overcomes these two major barriers.

The new approach provides high flexibility and precise control of the timing and amount of material applied. It is applicable for a wide range of matrix compounds. The general approach and critical instrumental parameters of the technique will be discussed, and its applicability for the enhancement of SIMS ion signals will be shown on examples of drug compounds and drug molecules embedded in tissue homogenate. We show that ion signals of clozapine could be enhanced by a factor of 3 for the protonated molecule $[M+H]^+$ by adding 2,5-dihydroxybenzoic acid (2,5-DHB), a common matrix compound used in MALDI. The $[M+H]^+$ ions of the drug molecules chloroquine and tamoxifen show an enhancement with 2,5-DHB matrix application. A factor of 7 enhancement of clozapine could be achieved with 3-nitrobenzonitrile (3-NBN), a species utilized for primary ion formation in the matrix assisted ionization vacuum (MAIV) technique. The abundance and intensity of lipid related signals (e.g., the phosphocholine fragment at m/z 184) in the spectra are significantly enhanced for the analysis of the tissue homogenate. The addition of formic acid shows another example for signal enhancement using the new approach, with an increase of the

$[M+H]^+$ signal of the drug molecule by a factor greater than 3 and of the phosphocholine signal (*m/z* 184) by a factor of 6.

4:20pm **AS-ThA7 ToF-SIMS Imaging of Bee Brain Tissue – Comparing Lipid Distributions and Varying Sample Preparation Methodologies*, Jordan Lerach*,** *E. Amsalem, C.M. Grozinger,* The Pennsylvania State University

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) with cluster-based primary ion sources enables researchers to elucidate molecular information from complex samples with sub-micron imaging resolution. This technique is becoming more commonly applied to complex biological systems due to its excellent molecular imaging capabilities. The following research details, with chemical specificity, the location of molecules of interest in brain tissue of the common eastern bumble bee (*Bombus impatiens)*. Microtomy was used to create thin tissue sections of both frozen-hydrated and freeze-dried tissues and the differences in the data sets are reported. A ToF-SIMS instrument with a Bi_n^{q+} primary ion source selected for Bi_3^{++} ions is used for analysis. This ion source is shown to produce large molecular ions in excess of 1,000 amu on the tissue samples which yields information from larger biomolecules such as lipids. In this analysis specific attention is paid to the lipid distribution since site-specific chemical imaging of lipids in the brain tissue remains relatively unexplored.

4:40pm **AS-ThA8 Understanding Matrix Effects in Mass Spectrometry*, Amy Walker*,** *L.D. Gelb,* University of Texas at Dallas

Chemical imaging methods, including imaging mass spectrometry (MS), are becoming widely used for the analysis of a variety of samples from biological tissues to electronic devices. A significant barrier to wider adoption of imaging mass spectrometry is the presence of matrix effects which complicate quantitative analysis. Interactions between an analyte molecule and its surroundings (the “matrix”) can substantially alter both the yield and type of ions observed. These matrix effects result in both significant nonlinearity of signal intensity with concentration and changes in the characteristic spectrum of a given species with environment. We present progress towards the quantitative extraction of chemical concentration profiles, component spectra, sample topography, and other information from imaging mass spectrometry data in the presence of matrix effects. Our approach is based on maximum *a posteriori* (MAP) reconstruction against physically motivated models rather than statistical dimensionality-reduction techniques such as Principal Components Analysis. We demonstrate our methodology using several different samples as well as synthetic data sets. These include systems that demonstrate “weak” matrix effects, such as mixed self-assembled monolayers, and “strong” matrix effects such as those observed in ionic liquid matrix enhanced secondary ion mass spectrometry.

5:00pm **AS-ThA9 Reducing Matrix Effects in Organic Secondary Ion Mass Spectrometry*, Lars Breuer*,** *H. Tian, N.J. Popczun,* The Pennsylvania State University*; A. Wucher,* University of Duisburg-Essen, Germany*; N. Winograd,* The Pennsylvania State University

Secondary ion mass spectrometry (SIMS) is a powerful tool for surface analysis. With the development of cluster ion beams, this technique now has the capability to analyze organic materials while maintaining molecular information of the analyte. A challenging aspect in SIMS applications in multi-components systems are so called *matrix effects* in the ionization probability of sputtered material. Unfortunately, there is no theory to date which is capable of predicting these matrix effects. Results are presented here to show one physical and one chemical approach to address and reduce matrix effects in an organic model systems of Irganox 1010 and 1098.

The first, and perhaps most straightforward approach in overcoming matrix effects is to decouple the ionization from the sputtering process. For this purpose, the plume of sputtered material above the sample, mainly consisting of neutral species, is intersected with an intense ultrafast laser pulse in the near infrared region with power densities up to several 10^{15} W/cm^2. This pulse ionizes neutral particles within the plume and makes their detection feasible

The second approach presented is based upon the idea of enhancing protonation at the bombardment sites. HCl doped Ar_n^+ gas cluster ions, in which the HCl molecules are incorporated into the gas clusters, are used as the primary ion beam. During analysis, H_2O is precisely leaked into the analysis chamber while the sample is cooled with liquid nitrogen. In this way, a thin ice overlayer is formed at the sample surface to facilitate the dissociation of the HCl molecules incorporated in the Ar_n gas clusters. The free hydronium ions become available at the impact site, which aid the protonation of intact molecules. During the entire analysis, a dynamic equilibrium between deposition and sputtering of ice is well maintained to yield a quantitative depth profile.

5:20pm **AS-ThA10 Image Fusion for Improving the Visualization of Elemental and Isotopic Distributions in SIMS*, Jay Tarolli*,** *B. Naes, B. Garcia, A. Fischer, D. Willingham,* Pacific Northwest National Laboratory

While secondary ion mass spectrometry (SIMS) is a technique that offers a substantial amount of chemical information of an analysis area, it comes with inherent limitations that often reduce the signal-to-noise ratio of desired species as well as the achievable spatial resolution. A growing approach to overcoming these limitations is to acquire complementary information from other analytical imaging techniques, such as optical and electron microscopy. Image fusion is a post-acquisition data analysis technique that has been recently applied to new and more diverse SIMS experiments in order to improve the perceived spatial resolution, intensity, and contrast of chemical images. The basis of image fusion is to combine information from two or more input images in order to create an output visualization that better represents the analysis area than any of the input images could alone. Thus, multimodal imaging analyses that incorporate SIMS and a second higher resolution analytical technique, followed by post-acquisition image fusion, are able to provide a representation of chemical information with greater detail at a smaller scale.

In this work, a new source of higher resolution data, X-ray energy-dispersive spectroscopy (EDS), is explored to improve the visual quality of SIMS images, combining elemental information with chemical information. First, a workflow was developed to register and fuse EDS images of an Al-Si-Cu alloy at various microscope magnifications with dynamic SIMS images to better visualize the localization of Cu and Si domains. A new implementation of image fusion was then developed to improve the screening process of U-bearing particles. In this case, elemental information provided by EDS is used to improve the spatial resolution of uranium isotopic distributions in order to differentiate particles which may potentially be enriched. These particles can then be screened individually to verify the isotopic distributions. In this case, image fusion has been applied not simply in a proof-of-concept scenario, rather an implementation that improves an existing process in order to obtain SIMS results with higher accuracy and precision.

5:40pm **AS-ThA11 Evaluating the Utility of Uranium-Molybdenum Foils as Nuclear Fuels via Elemental and Isotopic Imaging*, David Willingham*,** *J. Tarolli, B. Naes, M. Rhodes, M. Dahl, A. Guzman, D. Burkes,* Pacific Northwest National Laboratory

We aim to characterize the elemental and isotopic composition of uranium (U) metal and U metal alloys by electron microscopy (EM) and secondary ion mass spectrometry (SIMS). This type of characterization is important in understanding the behavior and performance of nuclear fuels and targets, and could potentially be utilized to interrogate processing history of the material. One example of such nuclear alloys is the uranium-molybdenum (U-Mo) system, development of which is being actively pursued throughout the world for use in research and test reactors (NA-23 Reactor Conversion Program), light water power reactors (DOE-NE Accident Tolerant Fuel), and pulse reactors (DoD – Army).

Previous EM characterization of approx. 19.75% enriched ^{235}U-10wt% Mo fuel foils produced for the NA-23 Reactor Conversion Program revealed a complex grain structure of coarse, highly elongated regions interspersed with finer, more equiaxed grains. The distribution of grains was also organized within regions containing significant Mo variation produced during casting of this particular alloy. During post-irradiation examination, these regions and structures have been observed to behave differently depending upon the irradiation conditions that the fuel was subjected to. Elemental and isotopic heterogeneities in the fuel, particularly at boundaries between grains, have been hypothesized to lead to non-uniform swelling regions (i.e., volume growth) within the fuel. Understanding the elemental and isotopic distribution of alloying metals and other impurities is important to reasonably predict behavior of the fuel in a particular reactor system, ultimately enabling successful qualification for its use.

SIMS image analysis revealed several key characteristics of the U-Mo foil system. First, Mo rich grains could be observed by SIMS imaging. These grains are highly elongated along the length of the foil. Secondly, carbon inclusions, likely a result of U carbides, were found in the SIMS images. These inclusions can be seen to track with the previously observed Mo rich elongated grains. Finally, the U within the foil is much more homogenized than the Mo and appears to be much less mobile. The ^{235}U/^{238}U is consistent with the known value at approx. 20% enrichment of ^{235}U and the

U isotopic distribution is homogenous in all regions of the U-Mo foil. It is, therefore, likely that non-uniform swelling of these foils under irradiation is due primarily to U-Mo elemental heterogeneities rather than U isotopic variations.

6:00pm **AS-ThA12 Investigation of the Interaction Between a High Poly Vinylpyrrolidone Content Silicone Hydrogel Contact Lens and a Natural Humectant using Surface Imaging Techniques***, **Katarzyna Wygladacz**, D.J. Hook,* Bausch + Lomb

Background: Optimum surface wettability and high water content are both important factors that can influence successful contact lens wear. In the case of the silicone hydrogel contact lens, samfilcon A, polyvinylpyrrolidone (PVP) was engineered into the material to increase the water content and provide a wettable lens surface. As a compliment to high level of PVP in the lens chemistry another way to improve lens wettability is to take advantage of interactions between the lens material and the lens care solution. This study assessed the interaction of hyaluronate (HA), a natural humectant, present in Biotrue multi-purpose solution (MPS) with the high PVP-content samfilcon A lens, using multiple analytical techniques.

Method: X-ray Photoelectron Spectroscopy (XPS) characterization was used to confirm the presence of HA on the lens surface.The distribution of HA over the samfilcon A surface was assessed by quantitating lens surface roughness (RMS), before and after incubation with 0.1% (w/v) HA by atomic force microscopy (AFM) imaging. Confocal laser scanning (CLSM) and differential interference contrast (DIC) microscopies were used to characterize the association of HA to the surface of samfilcon A lenses after exposure to 0.1% (w/v) HA and HA present in Biotrue MPS.

Results: Differences in the XPS C1s spectra recorded for samfilcon A before and after exposure to 0.1% (w/v) HA were detected. Samfilcon A surface roughness (RMS) was 2.5 ± 0.4 nm before exposure to HA and was significantly decreased after incubation with 0.1% (w/v) HA, (RMS=0.6 ± 0.1nm; $p<0.05$). CLSM and DIC imaging illustrated a comparable confluent, stained HA network that extended across the entire surface with 0.1% (w/v) HA and commercial HA-containing MPS.

Conclusion: XPS analysis show evidence for samfilcon A surface modification with hyaluronate. CLSM and DIC imaging offered a comprehensive view of the lens surface and demonstrated an extensive coverage of HA on samfilcon A. AFM measurements confirmed that HA adsorption reduced roughness of the lens surface. Together, the combination of imaging techniques provided a unique picture of the interaction of HA and PVP containing silicone-hydrogel lenses.

Spectroscopic Ellipsometry Focus Topic
Room 104C - Session EL+AS+BI+EM+TF-ThA

Optical Characterization of Nanostructures and Metamaterials (2:20-3:40 pm)/Application of Spectroscopic Ellipsometry for the Characterization of Thin Films (4:00-6:00 pm) and Biological Materials Interfaces

Moderators: Tino Hofmann, University of North Carolina at Charlotte, Stefan Zollner, New Mexico State University, Heidemarie Schmidt, Technische Universität Chemnitz, Germany

2:20pm **EL+AS+BI+EM+TF-ThA1 Optical Properties of (Self-assembled) Nanostructured Surfaces Studied by Spectroscopic Mueller Matrix Ellipsometry and Local Direct Imaging Techniques***, **Morten Kildemo,*** Norwegian University of Science and Technology, Norway **INVITED**

This paper covers several applications of ex-situ and in-situ Spectroscopic Mueller Matrix Ellipsometry (SMME) for the study of self-assembled nanostructured surfaces, with applications ranging from antireflection coatings, PV-absorbers, nanoimprinting masks, plasmonic polarizers, plasmonic meta-materials and in particular hyperbolic metamaterials and meta-surfaces. The optical analysis is systematically supported by AFM, SEM and TEM. As nanostructured surfaces are often inherently anisotropic, SMME with variable angle of incidence and full azimuthal rotation of the sample is shown to be a powerful optical technique to fully characterize such anisotropic and sometimes bi-anisotropic materials. The first part of the presentation briefly reviews an uniaxial effective medium approach to model the kinetics of the optical response of self-assembled straight and tilted GaSb nanopillars [Le Roy et al., Phys. Rev. B 2010, Nerbo et al. Appl. Phys. Lett. 2009], and SiO_2–nanopillars containing plasmonic Cu [Ghadyani et al., Opt. Exp. 2013]. The second part of the presentation discusses the experimentally extracted uniaxial and biaxial optical properties of self-assembled plasmonic hyperbolic meta-materials [X. Wang et al., *Block-copolymer based self-assembled hyperbolic metamaterials in the visible range.* (manuscript in preparation), 2016] and metasurfaces [Aas et al., Opt. Expr. 2013]. Hyperbolic metamaterials use the concept of controlling the propagative modes through the engineering of the dispersion relation, and are considered highly promising to reach different meta-properties. The presentation is closed by the discussion of the fascinating Mueller matrix response of a highly organized array of hemispherical Au nanoparticles produced by Focused-Ion-Beam milling, and the response is discussed in the context of highly organized meta-surfaces and plasmonic photonic crystals [Brakstad et al. Opt. Express 2015]

3:00pm **EL+AS+BI+EM+TF-ThA3 Optical Properties of Nanocrystalline Si_3N_4:TiN Thin Films***, **Neil Murphy,*** Air Force Research Laboratory*; L. Sun,* General Dynamics Information Technology*; J.G. Jones,* Air Force Research Laboratory*; J.T. Grant,* Azimuth Corporation

Nanocomposite films comprised of mixed nitrides, especially Si-Me-N (Me=Ti, Zr, Hf), have generated significant attention due to their robust thermal and mechanical properties. In addition to their desirable structural characteristics, the mixing of dielectric Si_3N_4 with various metallic nitrides has the potential for the deposition of hybrid thin films with controllable optical absorption based on the fraction of metallic nitrides present within the Si_3N_4 matrix. In this work, nanocrystalline Si_3N_{-4} thin films, doped with varying amounts of TiN (1-20 at.%), are deposited using reactive magnetron co-deposition. Note that the Berg model for reactive sputtering is utilized to select the initial conditions for the deposition of the films, which are sputtered from elemental targets within a mixed nitrogen-argon environment and characterized *in-situ* using spectroscopic ellipsometry. The TiN content is varied through systematic adjustment of the current applied to the Ti cathode concurrent with pulsed DC deposition of Si_3N_4 at a constant current of 0.4 A. The use of -*in-situ*- ellipsometry, interrogating wavelengths from 381-1700 nm, allows for the real-time measurement of the refractive index, extinction coefficient, and thickness of the growing films. Additionally, *in-situ* ellipsometry data is used to observe the behavior of the films at the onset of growth, indicating the onset of Volmer-weber type nucleation. All ellipsometric data are fit using a Bruggeman effective medium approximation, varying the amount of TiN present within the films. Optical characterization of the Si_3N_4:TiN thin films indicates that the refractive index at 550 nm decreases gradually from 2.05 to 1.99 as the TiN content is increased from 0-20 at%, while the extinction coefficient rises from 0 to 0.35. These films demonstrate strong absorption features starting from 550 nm out to 1500 nm, allowing for efficient absorption of visible and near-infrared wavelengths. Variation of the TiN content within Si_3N_4:TiN films allows for the user to select the magnitude of extinction coefficient and refractive index, leading to potential applications as mechanically robust layers in interference filters, or as alternatives to lossy metallic configurations in plasmonic devices.

3:20pm **EL+AS+BI+EM+TF-ThA4 The Effect of Aluminum Content on Properties of Al-doped Zinc Oxide Thin Films Grown at Room Temperature***, **Lirong Sun,*** General Dynamics Information Technology*; N.R. Murphy,* Air Force Research Laboratory*; J.T. Grant,* Azimuth Corporation*; J.G. Jones,* Air Force Research Laboratory

Transparent conductive Al-doped zinc oxide (AZO) thin films have shown excellent structural, optical and electrical properties for applications in photovoltaic and optoelectronic devices, transparent conducting electrodes, solar cells, liquid crystal displays, touchscreens, energy efficient window coatings and heat reflective coatings. In this work, the AZO thin films were deposited at room temperature by multi-target reactive magnetron sputtering using metallic Zn and Al targets simultaneously. The Al doping content of the AZO films by x-ray photoelectron spectroscopy (XPS) had great impacts on optical properties in the near infrared (NIR) and in the UV regions and were strongly correlated to their electrical properties. The spectroscopic ellipsometry data in three incident angles and transmission intensity data were measured and fitted simultaneously with a Tauc-Lorentz oscillator and a Drude model in the wavelength of 270 -2500 nm. The transmittance and reflectance spectra, the derived refractive index and extinction coefficient, were tailored in the NIR region by Al content and correlated to the electrical resistivity. The blue shift of the absorption edge in the UV region and the widening of the optical band gap were associated with the increase of the Al content. Structural, optical and electrical properties were characterized using x-ray diffraction, scanning electronic microscopy, UV-Vis-NIR spectra and four-point probe methods.

4:00pm **EL+AS+BI+EM+TF-ThA6 Optical Monitoring of Growth (and Death) of Thin Film Materials for Solar Cells*, Nikolas Podraza*,** *K. Ghimire, M.M. Junda, A.A. Ibdah, P. Koirala,* University of Toledo*; S. Marsillac,* Old Dominion University*; R.W. Collins, Y. Yan,* University of Toledo **INVITED**

Performance of thin film solar cells depends on (i) electronic quality of the components (doped and undoped semiconductors, metallic and transparent conducting contact layers), (ii) component optical response, and (iii) full opto-electronic response of the photovoltaic (PV) device structure dictated by layer properties and thickness. Spectroscopic ellipsometry probes (ii) and (iii) through measurement of both thickness and optical response ($N = n + ik$, $\varepsilon = \varepsilon_1 + i\varepsilon_2$, $\alpha = 4\pi k/\lambda$) of multiple layers in thin film device structures. Assessing (i) electronic quality of materials or devices optically relies on understanding other property information deduced from the optical response, such as connecting variations in film structure (crystallinity, degree of disorder) or growth evolution to device performance. In situ, real time spectroscopic ellipsometry (RTSE) monitors growth evolution and post-deposition processes to better understand property changes with thickness, phase transitions and separation, and process kinetics. RTSE of hydrogenated silicon (Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS) absorbers have been used to understand growth and its relationship to the respective device performance. All of these are relatively mature PV technologies, where knowledge gained from RTSE during growth can potentially improve metrology and manufacturing. The potential impact of RTSE is equally strong when applied to developing technologies. Organometal lead halide perovskite semiconductors ($CH_3NH_3PbI_3$) are used in >20% initial efficiency solar cells but suffer from degradation with temperature, bias, moisture, and ultraviolet light exposure. The time scale of device performance degradation is much shorter than that of other polycrystalline PV (CdTe, CIGS). RTSE has been applied during co-evaporation of CH_3NH_3I and PbI_2 to produce the perovskite, but also during decomposition of the perovskite. Significant fractions of CH_3NH_3I and PbI_2 at the substrate / perovskite and perovskite / ambient interfaces after deposition even under simple atmospheric exposure begin to appear in a matter of minutes. The ability to track the degradation – or death of this material – in addition to growth may be equally important to assessing the ultimate stability and manufacturability of these next generation PV materials.

4:40pm **EL+AS+BI+EM+TF-ThA8 Monitoring Nanometer-Thin Film Formation using Ellipsometry*, Bert Müller*,** *F.M. Weiss, T. Töpper, B. Osmani,* University of Basel, Switzerland

Elastomers can transform electrical energy into mechanical one. They have a wide variety of appli-cations including powering wipers, sound generation, and operating camera lenses. Sandwiched between electrodes the deformable but incompressible elastomer laterally expands when apply-ing a voltage. To provide the necessary strain of at least 10 %, micrometer-thick silicone mem-branes need an operation voltage of several hundred volts, which is inappropriate for the human body. Nanometer-thin membranes, however, require only a few volts. To generate forces as nec-essary for artificial sphincters, i.e. muscles to treat incontinence, several ten thousand membranes have to be sandwiched. Currently, the manufacturing methods such as organic molecular deposition only reach deposition rates of about one micrometer per hour, which does not allow fabricating the sandwiched nanostructures in an efficient way. We have developed an alternative deposition method to pre-pare extremely flat silicone membranes that are below one micrometer thick. The root-mean-square-roughness is smaller than one nanometer. For this purpose, silicone polymers in solution are sprayed by electrospray deposition [1,2]. Usually electrospraying is based on direct current mode. Here, we have employed, however, an alternating current to avoid charge accumulation on the substrate. Spectroscopic ellipsometry has been used to monitor the formation of confluent organic films and electrodes as well as the changes of the organic thin films during ultra-violet radiation treatments. This in situ technique enabled us to derive the refractive index, the porosity, the surface rough-ness, and the film thickness. The derived quantities on surface roughness and film thickness were validated using atomic force microscopy. The combination of electrospraying, ultra-violet light curing, and in situ ellipsometry has a huge potential to efficiently create and monitor nanometer-thin, ultra-flat elastomeric membranes, which may become part of artificial muscles for medical applications and beyond.

[1] F.M. Weiss, T. Töpper, B. Osmani, S. Peters, G. Kovacs, and B. Müller Electrospraying Nanometer-Thin Elastomer Films for Low-Voltage Dielectric Actuators Advanced Electronic Materials (2016) 1500476; DOI: 10.1002/aelm.201500476

[2] F.M. Weiss, T. Töpper, B. Osmani, H. Deyhle, G. Kovacs, and B. Müller Thin Film Formation and Morphology of Electro-sprayed Polydimethylsiloxane Langmuir 32 (2016) 3276-3283

5:00pm **EL+AS+BI+EM+TF-ThA9 Optical Determination of Electrical Response for Thin Film Transparent Conductors: Spectral Range Dependence*, Prakash Uprety*,** *M.M. Junda, K. Lambright, R. Khanal, A. Phillips, M. Heben, D. Giolando, N.J. Podraza,* University of Toledo

Thin films with simultaneous high transparency and electrical conductivity have applications in photovoltaics, displays, and other opto-electronic devices. Accurate characterization of electrical transport properties along with optical properties in these transparent conductors, particularly when in the device structure, is of critical importance to their use. Spectroscopic ellipsometry (SE) provides a widely applicable method for determining such properties without many of the complications and limitations that accompany other methods that make use of physical contact to the film. As is described by the Drude model, free carrier optical absorption has increasing effect on the complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) with decreasing photon energies. Thus, extracting ε from SE measurements spanning the visible to terahertz (THz) frequency ranges provides sensitivity to film thickness and morphology at higher energies and free carrier absorption dominating the optical response at low energies. In this work fluorine doped tin oxide (SnO_2:F), aluminum doped zinc oxide (ZnO:Al), and sprayed single walled carbon nanotube (CNT) thin films are measured with ex situ SE over a spectral range of 0.035 to 5.9 eV using a single rotating compensator multichannel ellipsometer (0.75 - 5.9 eV) and a single rotating compensator Fourier transform infrared ellipsometer (0.035 - 0.75 eV). Additionally, the ZnO:Al and CNT films are measured using a single rotating compensator THz ellipsometer (0.4 - 5.8 meV) to further extend the measured spectral range to lower energies. Due to the wide spectral range measured, a single model describing ε and layer thicknesses has sufficient sensitivity to simultaneously determine electronic transitions, vibrational phonon modes, and free carrier absorption. The electrical properties in the Drude model are described by the bulk material resistivity ρ and scattering time τ. Optically extracted ρ has increasing correspondence to ρ deduced from four point probe electrical measurements as increasing low photon energies are included in the fitting (< 5% variation in ρ for ZnO:Al analzying the full measured range); a behavior that demonstrates the benefit of extending the measurement spectrum to very low energies. The analyzed spectral range dependence of optically determined transport properties in these examples is considered to illustrate how narrower spectral range measurements impact deduced ρ and τ.

5:20pm **EL+AS+BI+EM+TF-ThA10 Spectroscopic Ellipsometry Studies of CdS-CdSe-CdTe Alloys: Applications in Thin Film Solar Cells*, Maxwell Junda*,** *C.R. Grice, Y. Yan, N.J. Podraza,* University of Toledo

Recent studies have demonstrated that photovoltaic (PV) device performance of thin film cadmium telluride (CdTe) solar cells is improved when a thin cadmium selenide (CdSe) layer is added at the cadmium sulfide (CdS) / CdTe interface and when oxygen is added to the CdS window layer (CdS:O). Specifically, devices fabricated with this configuration show increased short circuit current density without a corresponding degradation in open circuit voltage. The high temperature close spaced sublimation (CSS) deposition of the CdTe layers in these devices effectively anneals the existing CdS:O / CdSe window layer creating alloyed regions between these three materials as opposed to distinct, separate layers at the front side of the device. To better understand the sources of performance gain, we begin by using ex situ spectroscopic ellipsometry (SE) from the near infrared to the ultraviolet (0.74 – 5.9 eV) to study the optical and structural properties of these alloys. Films of CdS:O, CdS_xSe_{1-x}, and $CdSe_yTe_{1-y}$ are fabricated on soda lime glass substrates by radio frequency sputtering a stack of layered combinations of CdS, CdSe, and/or CdTe followed either by annealing at the CdTe CSS deposition temperature or actual CSS of CdTe. A parameterized model describing the critical point transitions in the optical response ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) is developed, allowing for tracking of the changes in ε as a result of film composition and processing for each alloy. Additionally, structural and compositional variations introduced by the alloying of materials is considered and supported by complementary x-ray diffraction and energy dispersive x-ray spectroscopy measurements. The database of ε developed for these materials can be used to assess how the oxygen introduced in the CdS:O layer and diffusion of CdSe into both CdTe and CdS:O modify that interface and impact PV device performance.

5:40pm **EL+AS+BI+EM+TF-ThA11 Development of Growth Evolution Diagrams for RF Sputtered Nanocrystalline Hydrogenated Silicon Thin Films via Real Time Spectroscopic Ellipsometry***, **Dipendra Adhikari**, M. M. Junda, N. J. Podraza,* University of Toledo

As a result of its increased visible light absorption and increased stability in comparison to hydrogenated amorphous silicon (a-Si:H), hydrogenated nanocrystalline silicon (nc-Si:H) thin films are of considerable interest for a variety of opto-electronic applications, including photovoltaic (PV) devices. Radio frequency (RF) sputtering in an Ar + H_2 ambient provides a cost effective deposition technique for Si:H films and has advantages over conventional plasma enhanced chemical vapor deposition as a result of the potential to improve deposition rates and the elimination of hazardous precursor gasses. In this work we investigate how pressure, RF power, and Ar/H_2 ambient gas composition ratio influence film structure (thicknesses; amorphous, nanocrystalline, mixed phase composition) and optical response of Si:H films deposited by RF sputtering onto native oxide covered crystalline silicon wafer substrates using in situ real time spectroscopic ellipsometry (RTSE) over the near infrared to ultraviolet spectral range. Through analysis of RTSE measurements and application of virtual interface analysis where appropriate, the time evolution of bulk layer thickness, surface roughness, and complex dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) spectra are extracted. Variations in nucleation and evolution of crystallites forming from the amorphous phase as a function of pressure, power, or Ar/H_2 ratio can be deduced from the growth evolution and used to create growth evolution diagrams. Overall film quality, crystallinity, and hydrogen incorporation (assessed using infrared extended measurements), are also determined from ε. X-ray diffraction measurements provide complementary information about how deposition conditions influence the density, size, and preferred orientation of crystallites. In addition to controlling film phase and structure, improvement of the deposition rate is also of practical interest and is explored here.

Surface Science
Room 103C - Session SS+AS-ThA

Celebrating a Life in Surface Science: A Symposium in Honor of JOHN T. YATES, JR.

Moderators: John Russell, Jr., Naval Research Laboratory, Vincent Smentkowski, General Electric Global Research Center

2:20pm **SS+AS-ThA1 Introductory Remarks About Prof. John T Yates Jr. and his Scientific Legacy***, V. Smentkowski,* General Electric Global Research Center*; **John Russell**,* US Naval Research Laboratory

Introductory remarks about Prof. John T Yates Jr. and his scientific legacy

2:40pm **SS+AS-ThA2 JOHN T. YATES, JR. - The Energizer Bunny (Invited Talk)***, **J. William Gadzuk**,* NIST

My friend and colleague John Yates was a joy to share life with. His perpetual enthusiasm, imagination, and sincere interest in whatever happened to be the topic of the moment whether a complex issue in surface science, the fate of an astronomically distant galaxy, the program for Lorin Maazel's next Pittsburgh Symphony concert, the well-being of his scientific "children" and real family, or speculation on what's likely to be tonight's specialties on the menu of our favorite Il Pizzico Restaurant near NIST, was infectious. John's retirement in 2006 from his chair at the University of Pittsburgh [which he went to from NBS/NIST in 1982] brought him to an emeritus-like guest faculty desk at the University of Virginia. Soon upon settling in at the university, his "desk" became an office became a full-fledged surface science lab with an active group of students and post docs supported by research grants that totaled among the highest within UVA chemistry, all of which was built up from scratch after John "retired". He was the only person I know who confessed that he really liked writing research proposals. He lived and executed his retirement with more excitement, energy, and enthusiasm than a young, tenure-seeking assistant professor; the energizer bunny personified.

I will present a number of anecdotal/amusing illustrative vignettes drawn from my experiences with "the energizer bunny" and discuss why his seminal JCP papers on thermal broadening in ESD [**51**,1264(1969)] and on resonance ESD [**90**,5793(1989)] were so influential in my own conceptualization and realizations in surface dynamics.

Finally, John and I had the privilege of being co-participants in two NIST Oral History interviews in 2014 and 15, once as a "target" and then as an interviewer [of each other]. This was a great way for us to summarize our nearly half a century of being a part of each other's life, a privilege that I feel very fortunate and honored to have had. [transcripts available upon request: gadzuk@nist.gov [mailto:gadzuk@nist.gov]]

3:00pm **SS+AS-ThA3 Polymer Precursors Studied by Mass Spectrometry, Ion Mobility and Computational Strategies (Invited Talk)***, **David M. Hercules**,* Vanderbilt University

There has been considerable interest recently in using mass spectrometry and related methods to address structures of complex systems, including block copolymers. Polyurethanes (PURs) are polymers that contain multiple "hard" and "soft" blocks that have different sequences of the same units along the chain. The ultimate goal in studying such materials would be the ability to determine the exact sequence along the chain and to correlate specific sequences with polymer performance. We have established a protocol on smaller molecules that can address this type of issue using the combination mass spectrometry, collision-induced dissociation, ion mobility spectrometry (IMS), and molecular dynamics simulations. A key component of the of the project is the synthesis of model PUR oligomers having authentic component sequences. The individual components are methylene diphenyl diisocyanate (MDI), bis-diol terminated polybutylene adipate (PBA), and 1,4-butane diol (BD), each containing 3 MDIs, 4 PBAs and 4 BDs (MW = 1910). The main collision-induced dissociation fragmentation reactions occur between the PUR and PBA carbonyl groups and BD hydrogen atoms. Additionally, a 1,3 H-shift reaction occurs between the PUR N-H group and BD oxygen. Different fragment ions are observed depending on the unit size and the sequences of the units in the chain. An important aspect of the research is to use IMS to separate compounds that have identical masses but different molecular-ion scattering cross sections. Computational strategies are important for calculation of IMS collisional scattering cross sections and to aid in the interpretation of fragmentation mechanisms. They help to identify synthetic targets that will show the largest effects of the experimental measurements.

3:20pm **SS+AS-ThA4 From Symmetry to Applications: One of Many Journeys Touched by John Yates (Invited Talk)***, **Ellen Williams**,* Advanced Research Projects Agency - Energy

In the 1970's John Yates spent a sabbatical year at Caltech, where he touched the lives of many students and postdocs working in the group of Prof. Henry Weinberg. My story starts as a young student, fascinated with symmetry and statistical mechanics, who was privileged to work in the laboratory with John, in those early days of surface science when it seemed that every observation opened new horizons.

I will provide highlights of some of the exciting research that followed from those early days of surface science, discussing the impact of scanning tunneling microscopy, the linkages of surface science and nano-electronics, and the practical impacts of many years of fundamental studies from the perspectives of industry and ARPA-E.

4:00pm **SS+AS-ThA6 A Tribute to John T. Yates Jr. and His Pioneering Work with Graphitic Surfaces (Invited Talk)***, **Patricia A. Thiel**,* Ames Laboratory

John T. Yates, Jr. directed pioneering work on graphitic surfaces. In one case, he and his group prepared graphene on SiC surfaces long before graphene was popularized. In another case, they developed a method to induce surface intercalation of Cs at a graphite surface. In this talk, I will review his contributions and describe the ways in which his work has inspired some of my own. For instance, we have studied adsorption, nucleation, growth, and reaction of dysprosium (Dy) on the basal plane of graphite, and the way that these phenomena are influenced by surface defects. Dysprosium islands nucleate homogeneously on terraces at room temperature. With increasing temperature the shape changes, with islands becoming taller and more facetted. At still higher temperature, Dy reactions with graphite to form carbide. Using the technique developed by John and his group, we can also induce surface intercalation at elevated temperature. We show that this surface intercalation differs significantly from bulk intercalation.

4:20pm **SS+AS-ThA7 Surface Science influenced by Dopants (Invited Talk)***, **Hajo Freund**,* Fritz Haber Institute of the Max Planck Society, Germany

Model systems are useful to establish structure/morphology reactivity relations in heterogeneous catalysis. Here we use a Metal-Insulator-Metal (MIM) structure to advice CO_2.

We had shown before that ultra-thin oxide films could be used as effective barriers to charge Au islands with electrons from the metal below the support. The idea is to use the electrons stored in the islands to activate molecules by electron transfer. Such a molecule is the energy economy relevant carbon-dioxide for example. We demonstrate adsorption of CO_2 at gold islands and the reversible formation of CO_2 anions and oxalates based on information from microscopy and spectroscopy.

We show how to transfer those ideas developed for thin film systems to bulk materials, where we use appropriate dopants within the support material to provide the electron source. The electron transfer to Au islands as well as the activation of oxygen will be demonstrated.

4:40pm **SS+AS-ThA8 Desorption: Out of the Vacuum, into the Liquid (Invited Talk)**, ***Michael Grunze,*** KIT, Germany; *H.J. Kreuzer,* Dalhousie University, Canada

The first paper on thermal desorption John Yates published with Ted Madey was entitled: *Nitrogen Desorbs with Complex Kinetics*. Thermal Desorption Spectroscopy, in more and more sophisticated experimental set-ups including flow reactors, became then a prominent techniques in John´s Laboratory to study simple and complex surface chemical reactions. In this short report, we look further into "complex kinetics" and find that the theoretical framework of a thermally activated process can not be applied to the detachment of particles in a micro-fluidic shear-flow experiment.

The theoretical description of the desorption process treats bond breaking as a thermally activated process, which can be described by the Arrhenius equation. The activation energy and the pre-exponential factor can be determined from a series of TPD experiments with either varying coverage or at constant coverage, using different heating rates. Here we experimentally and theoretically analyze the detachment of microscopic polystyrene beads from different self-assembled monolayer (SAM) surfaces in a shear flow to develop a mechanistic model for the removal of cells from surfaces. The detachment of the beads from the surface is treated, as in thermal desorption experiments, as a thermally activated process to determine activation barrier and attempt frequency of the rate determing step in bead removal. The statistical analysis of the experimental shear detachment data, obtained in phosphate-buffered saline solution, results in an activation energy of detachment around 20 kJ/mol. This value is orders of magnitude lower than the adhesion energy measured by atomic force microscopy (AFM). The same order of magnitude for the adhesion energy measured by AFM is derived from ab initio calculations of the van der Waals interaction energy between the polystyrene beads and the SAM-covered gold surface. We hence conclude, that the rate determing step for detachment of the beads is the initiation of rolling on the surface (overcoming static friction), and not physical detachment as would be the case in a gas desorption experiment.

5:00pm **SS+AS-ThA9 Infrared Spectroscopy in Surface Science: The Legacy of John T. Yates, Jr. (Invited Talk)**, ***Michael Trenary,*** University of Illinois at Chicago

A constant theme throughout the long scientific career of John T. Yates, Jr. was the use of infrared spectroscopy to probe the properties of surfaces and of adsorbed molecules. In his very first publication in 1961, based on his PhD thesis from MIT, he used transmission infrared spectroscopy to study the interaction of carbon monoxide with alumina-supported nickel surfaces. He continued to use innovative methods of transmission infrared spectroscopy in his laboratories at the National Bureau of Standards, the University of Pittsburgh, and the University of Virginia. The final publication of his career, which appeared in 2016, featured transmission IR spectra of CO interacting with the surfaces of titania-supported gold. In addition to transmission IR spectroscopy of high-area powdered samples, he was also a leader in the use of reflection absorption infrared spectroscopy (RAIRS), also known as infrared reflection absorption spectroscopy (IRAS), a method that allows IR spectra to be obtained on small-area metal single crystals. RAIRS is one of the few surface science techniques that can be used both under UHV conditions as well as in the presence of an ambient pressure of gas. John Yates was a pioneer in bridging the so-called pressure gap by using RAIRS to probe gas-surface interactions in the presence of elevated gas pressures. Recent examples from other research groups will be presented to highlight the continuing impact John Yates has had in the use of infrared spectroscopy in surface science.

5:20pm **SS+AS-ThA10 From Surface Science to New Catalysts (Invited Talk)**, ***Ib Chorkendorff,*** Technical University of Denmark

In this presentation I will give a brief overview of how my post-doc with John T. Yates Jr. influenced my way of working and how that philosophy could be used too go from fundamental investigations of reactions on surfaces to actually understand and make new heterogeneous catalysts. First we shall discuss how mass-selected nanoparticles of CuZn alloys to elucidate the dynamics of the methanol synthesis catalysts. The produced nanoparticles will be compared to the conventional CuZnAl at 1 bar for synthesizing methanol from CO_2 and H_2 [1, 2, 3]. The methanol synthesis on CuZn will also be discussed with respect to our very recent findings of using alloys of NiGa for methanol synthesis [4]. The use of mass-selected nanoparticles will be further demonstrated for electrochemical Oxygen Reduction Reaction, which is really the limiting reaction in Proton Exchange Membrane Fuel Cells. Here we have found entirely new classes of electro-catalysts by alloying Pt with early transition metals [5] or the lanthanides [6]. We have also shown that it is possible to make mass-selected nanoparticles of these alloys with very good activities [7] and PtGd alloys [8].

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5:40pm **SS+AS-ThA11 Activation of Carbon Dioxide on Metal and Carbide Surfaces (Invited Talk)**, ***Jingguang Chen,*** Columbia University

Converting CO_2 into valuable chemicals and fuels is one of the most practical routes for reducing CO_2 emissions while fossil fuels continue to dominate the energy sector. The catalytic reduction of CO_2 by H_2 can lead to the formation of three types of products: CO through the reverse water-gas shift (RWGS) reaction [1], methanol via selective hydrogenation [2], and hydrocarbons through combination of CO_2 reduction with Fischer-Tropsch (FT) reactions. In the current talk we will discuss some of our recent results in CO_2 conversion [3]. Our research approaches involve the combination of DFT calculations and surface science studies over single crystal surfaces, catalytic evaluations over supported catalysts, and in-situ characterization under reaction conditions. We will also discuss challenges and opportunities in this important research field [4].

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6:00pm **SS+AS-ThA12 Thermodynamic Control of TTF-TCNQ Molecular Layers on Metallic Surfaces (Invited Talk)**, ***Petro Maksymovych***, Oak Ridge National Laboratory

Bulk molecular ionic solids exhibit a fascinating diversity of electronic ground states, including unconventional superconductivity. The electronic properties of these systems have historically avoided surface analytical studies due to the intrinsic difficulty with surface preparation. We are therefore pursuing epitaxial growth of charge-transfer compounds, toward understanding their fundamental properties and creating new kinds of metal-organic or organic-organic interfaces [1,2]. A primary challenge is to assure compatibility of supported epilayers with the redox processes so as to enable, enhance but not eliminate significant charge transfer and electron correlations with supported structures.

In this talk, I will discuss 2D molecular structures of TTF and TCNQ molecules supported on metal and graphitic surfaces. We established that these molecules self-organize into a "zoo" well-ordered structure with a wide-range of TTF:TCNQ ratios [3] - a marked deviation from a single stable 1:1 ratio in the bulk. We propose that the formation these structures is governed by a surface phase diagram that exhibits at least four distinct stable compositions. The diagrammatic picture explains many of the properties of such systems that often seem incidental: the morphology of epilayers, governed by nucleation and growth; coexistence and abundance of various phases, and the distinct molecular structure of phase boundaries. Using coupled image and computational analysis, we conclude that the observed shapes are dictated by the preferential formation of a well-defined “quad”-motif involving TTF(TCNQ) molecules coordinated by at least four of its matching neighbors. Thus enabled deterministic control is beneficial to both electronic properties of surface phases (which can develop local magnetic moments) and the formation of quasi-2D TTF-TCNQ solids, which develop decidedly non-bulk Mott-insulating state despite having 1:1 bulk ratio. We anticipate that these properties are quite general for multicomponent molecular compounds, providing new opportunities for self-organized and electronically interesting molecular systems.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

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Spectroscopic Ellipsometry Focus Topic
Room Hall D - Session EL+AS+EM+TF-ThP
Spectroscopic Ellipsometry Poster Session

**EL+AS+EM+TF-ThP1 FTIR Ellipsometry Studies of Thermally Grown GeO_2 on Ge*, Jaime Moya,* ***T.N. Nunley, N.S. Fernando, N. Samarasingha, S. Zollner,* New Mexico State University

To study the vibrational modes of GeO_2, we produced a set of thermal GeO_2 oxides ranging from 45 to 136 nm in thickness. Receiving a set of Ge Bulk wafers, we cleaved and roughened the back sides via an aluminum abrasive to avoid backside reflections. To remove carbon-containing surface contaminants and leave a stable oxide on the wafer, we performed a hybrid dry/wet clean. The dry clean was done by subjecting the wafer to an ozone clean in an ultrapure oxygen environment while heating the sample to 150°C for 1 hour, followed by a 30 minute incubation period. The samples were then cleaned ultrasonically for 20 minutes in deionized water followed by 20 minutes in isopropanol. No harsh chemicals were used. The samples were then dried with nitrogen and annealed at 270 kPa and 550°C in ultrapure oxygen for a few hours to achieve different oxide thicknesses.

Using Fourier-transform infrared ellipsometry, the ellipsometric angles ψ and Δ were measured from 250 to 6000cm^{-1} at several angles of incidence (60° to 75°). The infrared lattice absorption peak of the amorphous GeO_2 was fit with a Lorentz oscillator.

When comparing our results to Lippincott's *et al.* [1] transmission measurements of vitreous GeO_2 formed by quenching hexagonal GeO_2, we see a negative shift in vibrational frequency. The difference can be attributed to the different Ge-O bond length comparing the vitreous GeO_2 and our amorphous thermal oxide. Our amorphous thermal oxide GeO_2 samples have a longer bond length, corresponding to a weaker bond and a lower vibrational frequency. This shift also shows a lower density of our samples compared to Lippincott *et al* [1].

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EL+AS+EM+TF-ThP2 Anisotropic Bruggeman Effective Medium Approach for Modeling Spectroscopic Ellipsometry Data of Porous Samples*, Stefan Schöeche,* *J. VanDerslice, J.A. Woollam,* J.A. Woollam Co., Inc.

Porous materials are widely used with applications including filtration devices, low-k dielectrics, catalysts, optical coatings, and more. The porous medium is described by its total porosity, pore diameter and specific surface area. The overall properties of the porous material are a result of the combined constituents and can often be approximated using effective medium theories. Due to complicated microstructure, these effective properties may vary along different directions or within the material resulting in anisotropic optical properties or gradients in pore size and total porosity.

Spectroscopic ellipsometry (SE) based porosimetry monitors the optical and structural changes of a porous sample during an adsorption and desorption cycle, i.e., insitu monitoring while the sample is exposed to an atmosphere with solvent partial pressure P varied between zero and the saturation vapor pressure of the solvent over flat surface P_0. Ellipsometric porosimetry based on the Lorentz-Lorenz equation is widely used to characterize thin porous films since it is simple (only requires refractive index at one wavelength) and the skeletal material refractive index is not needed for the calculation. However, the theory is based on invalid assumptions on the microscopic nature of the film, the choice of refractive index is random, it is applicable only to isotropic and homogeneous samples, makes assumptions on the filling of pores at relative pressures P/P_0=0 and P/P_0=1, ignores potential inaccessible pores, and does not provide access to the skeletal refractive index.

We present an alternative approach to analyze porous samples based on the anisotropic Bruggeman effective medium approximation (ABEMA). The model uses well established theory to best match the SE data over a wide spectral range, is easily extendable to more constituents, accounts for optical anisotropy due to the shape of the pores or the pore network, allows determination of the skeletal refractive index in unknown materials, is sensitive to inaccessible pores, and allows grading of relevant sample properties such as the total porosity. A comparison of the two model approaches for data obtained on a porous SiO_2 film on Si substrate will be shown.

EL+AS+EM+TF-ThP3 Optical Constants of M2-phase VO_2 Measured by Spectroscopic Ellipsometry*, SamuelT. White,* *R.F. Haglund, K. Hallman,* Vanderbilt University

Vanadium dioxide (VO_2) is a highly interesting material due to changes in its electronic and optical properties associated with the reversible phase transition from a monoclinic (M1) to a rutile (R) crystal structure. This transition makes VO_2 a promising candidate for many applications, including ultrafast electrical switching and optical modulation. There exists another, distinct monoclinic phase (M2) which also can undergo the transition to R, and which is structurally similar to a possible transient phase appearing in the M1-R phase transition. Thus, M2 is important to understanding the M1-R transition, besides being potentially useful for application in its own right; however, M2 and its phase transition are not as well-characterized as M1. Establishing the optical constants for M2-phase vanadium dioxide is an important step in characterizing this phase and will help provide understanding of its relationship to the other phases.

Here, variable-temperature spectroscopic ellipsometry is used to measure the optical constants of thin-film M2-phase VO_2 below and above the phase-transition temperature, for wavelengths ranging from 370 to 1690 nm. Samples were prepared by electron-beam deposition onto a silicon substrate, with Cr doping to prepare the M2-phase. Experiments were performed both at room temperature and at 95°C with a JA Woolam M-2000 Spectroscopic Ellipsometer equipped with a heated sample stage. VO_2 layer thickness was established by profilometry measurements, and the optical constants were extracted by fitting data to a sum of three Lorentz oscillators. The results are compared to those obtained for thin-film M1-phase VO_2.

The optical constants for M2 and M1 are found to have similar wavelength-dependence, and to agree generally with results obtained for M1 by other researchers. The extinction coefficient, k, is very close for both samples over all wavelengths measured. The index of refraction, n, on the other hand, is larger for M2 than for M1 by ~5-10% for almost all wavelengths measured, with the greatest difference occurring at wavelengths near the peak value, ~430 nm. At elevated temperatures, both samples show optical constants typical of R-phase VO_2, though the index of refraction again appears to be higher for the M2 sample than for the M1 sample. Repeating this experiment with samples prepared by another method may help to distinguish effects due to phase difference due to those due to other sample differences.

Spectroscopic Ellipsometry Focus Topic
Room 104C - Session EL+AS+EM+MI+TF-FrM

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Morten Kildemo, Norwegian University of Science and Technology, Nikolas Podraza, University of Toledo

8:20am **EL+AS+EM+MI+TF-FrM1 Magnetoopticalproperties of Metals, Half-Metals, and Garnets Probed by Vector-Magneto-Optical Generalized Ellipsometry***, **Heidemarie Schmidt**,* Technische Universität Chemnitz, Nano-Spintronics Group, Germany **INVITED**

Magnetotransport measurements are a standard technique for the electrical characterization of single layers on insulating substrates. However, magnetotransport measurements require electrical contacts and known current paths, which excludes application to multilayer stacks. Motivated by the recent development of fast Mueller matrix ellipsometers, we have set-up a vector magnetooptical generalized ellipsometer (VMOGE) with an 0.4 T octupole magnet [1] and have investigated magnetooptical response of a single layers and multilayer stacks in a magnetic field of arbitrary orientation and magnitude up to 0.4 T at room temperature. We assume that the off-diagonal element of the magnetooptical dielectric tensor of every magnetizable layer in the multilayer stack is a product of the magnetic field independent and wavelength dependent complex magnetooptical coupling constant and the magnetic field dependent and wavelength independent magnetization of the layer. As an example, the complex magnetooptical coupling constant of nominally 10, 20, and 30 nm thick ferromagnetic Ni films obtained from modelling corresponding VMOGE data is discussed. It was challenging to identify the magnetization direction of Ni films from different sets of magnetic field dependent Mueller matrix elements [2]. In the future knowledge of complex magnetooptical coupling constant of all magnetizable materials in a multilayer stack will allow for modelling and optimizing the magnetooptical response of given stack. As a second example, the modelled complex magnetooptical coupling constant of capped, ferromagnetic Fe, Ni20Fe80, Co, Ni80Fe20, and Ni thin films on ZnO substrates is discussed and related with the spin-dependent electronic bandstructure of given weakly correlated, magnetizable materials [3]. For this comparison the experimental complex off-diagonal elements of the magnetooptical dielectric tensor have been converted into theoretical complex off-diagonal elements of magnetooptical conductivity tensor. Finally, the experimental magnetooptical response of strongly correlated, magnetizable materials [4], e.g. half-metals and garnets, is presented and as an outlook development of new theoretical frameworks for calculating the bandstructure of such strongly correlated, magnetizable materials for a comparison with experiment is motivated. [1] K. M. Mok, N. Du, H. Schmidt, Rev. Sci. Instrum. 82 (2011) 033112; [2] K.M. Mok, C. Scarlat, G. J. Kovács, L. Li, V. Zviagin, J. McCord, M. Helm, H. Schmidt, J. Appl. Phys. 110 (2011)123110; [3] K.M. Mok, G. J. Kovács, J. McCord, L. Li, M. Helm, H. Schmidt, Phys. Rev. B 84 (2011) 094413; [4] G. Kotliar and D. Vollhardt, Physics Today 57 (2004) 53

9:00am **EL+AS+EM+MI+TF-FrM3 *In Situ* Terahertz Optical Hall Effect Measurements of Ambient Doping Effects in Epitaxial Graphene***, S. Knight,* University of Nebraska-Lincoln*; C. Bouhafs, N. Armakavicius, P. Kühne, V. Stanishev, R. Yakimova,* Linköping University, Sweden*; S. Wimer, M. Schubert,* University of Nebraska-Lincoln*; V. Darakchieva,* Linköping University, Sweden*; **Tino Hofmann**,* University of North Carolina at Charlotte

Recently, the cavity-enhanced THz optical Hall effect (THz-OHE) has been demonstrated as non-contact method to obtain free charge carrier properties using low-field permanent magnets [1,2]. A tunable, externally-coupled cavity is used to enhance the THz-OHE signal which allows the accurate determination of a sample's free charge carrier properties even at low magnetic fields. In this work we take advantage of this approach by integrating the permanent magnet into a gas flow cell. We demonstrate for the first time the application of the cavity-enhanced THz-OHE for the *in-situ* characterization of free charge carrier properties of monolayer graphene on Si-face 4H-SiC as a function of ambient conditions. The experiments were performed using a new rotating-analyzer THz ellipsometer at Linköping University. Upon changing the CO_2, H_2O, and O_2 concentration in the cell, large variations in both free charge carrier sheet density N_S and mobility μ are observed for the *n*-type graphene. The lowest N_S was found for the as-grown sample with $N_S = 5.9(1) \times 10^{11}$ cm^{-2} where $\mu = 2507(57)$ cm^2/Vs. The highest N_S was found after purging the sample with nitrogen for 6 hours with $N_S = 2.43(4) \times 10^{12}$ cm^{-2} where $\mu = 1604(23)$ cm^2/Vs. These significant changes are attributed to a redox-reaction of oxygen and water at the graphene surface which results in the extraction of electrons from graphene [3]. This will be discussed in detail in our presentation. We further observe that this doping mechanism is only partially reversible at room temperature upon removal of oxygen, carbon dioxide, and water by purging the cell with nitrogen. In conclusion, we demonstrate *in-situ* THz-OHE as a new and powerful technique to determine ambient-dependent doping mechanisms which is illustrated here using monolayer epitaxial graphene on Si-face 4H-SiC.

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[2] P. Kühne, C.M. Herzinger, M. Schubert, J.A. Woollam, and T. Hofmann, Rev. Sci. Instrum. **85**, 071301 (2014).

[3] A.N. Sidorov, K. Gaskill, M.B. Nardelli, J.L. Tedesco, R.L. Myers-Ward, C.R. Eddy Jr., T. Jayasekera, K.W. Kim, R. Jayasingha, A. Sherehiy, R. Stallard, and G.U. Sumanasekera, J. Appl. Phys. **111**, 113706 (2012).

9:20am **EL+AS+EM+MI+TF-FrM4 Excitons at Interfaces in Ellipsometric Spectra***, **Nuwanjula Samarasingha**, C. Rodriguez, J.M. Moya, N.S. Fernando, S. Zollner,* New Mexico State University*; P. Ponath, K. Kormondy, A. Demkov,* University of Texas at Austin*; D. Pal, A. Mathur, A. Singh, S. Dutta, J. Singhal, S. Chattopadhyay,* Indian Institute of Technology Indore, India

The presence of excitonic features in the optical constants and ellipsometry spectra of bulk semiconductors and insulators has been known for many years. In Si, Ge, and GaAs, the E_1 critical points are strongly enhanced by two-dimensional excitons, even at room temperature. Three-dimensional excitons have been seen in ellipsometry spectra for GaP and Ge. Excitons also influence the dielectric function of $SrTiO_3$. An exciton is an electron-hole pair bound by the Coulomb interaction, with properties similar to a hydrogen atom. The influence of excitonic absorption on the dielectric function was described by Tanguy.

In a thin epitaxial layer (with a thickness below or near the Bohr radius) on a substrate with a different band gap, the wave functions of the electron and hole are strongly modified. In a thin type-I quantum well, consisting of a narrow-gap semiconductor grown on a large-gap substrate, both the electron and the hole are confined, which leads to an increase in the dipole overlap matrix element. Therefore, the dominant absorption peak at 4.2 eV is larger in a 20 nm thick $SrTiO_3$ layer on a $LaAlO_3$ substrate than in bulk $SrTiO_3$. (The band gap of $LaAlO_3$ is larger than that of $SrTiO_3$.)

On the other hand, in a staggered type-II quantum well, either the electron is confined, or the hole, but not both. Therefore, the overlap dipole matrix element (and thus the excitonic absorption) is strongly reduced, because one quasiparticle resides in the quantum well and the other one in the substrate. If a $SrTiO_3$ layer is grown on Si or Ge, the valence band maximum occurs in the substrate, while the conduction band offset is very small. Therefore, the exciton wave function is delocalized (deconfined), which reduces the dipole overlap matrix element. Therefore, the real and imaginary part of ε of thin $SrTiO_3$ layers on Si or Ge are much smaller than in the bulk and decrease monotonically with decreasing thickness. A similar effect can be seen for thin ZnO layers on Si as a function of thickness.

The dielectric function of $SrTiO_3$ is not only affected by layer thickness. A very thick polycrystalline $SrTiO_3$ layer on Si has a much lower dielectric function than a single-crystalline $SrTiO_3$ substrate. In this case, we speculate that the magnitude of the dielectric function is related to other Tanguy parameters, perhaps the excitonic binding energy or the exciton decay rate (broadening). To investigate this further, we will perform temperature-dependent ellipsometry measurements on bulk zinc blende GaP, which has a much simpler band structure than wurtzite ZnO or the correlated metal oxide $SrTiO_3$, but shows similar excitonic effects.

9:40am **EL+AS+EM+MI+TF-FrM5 Infrared and Visible Dielectric Properties of $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$***, **Jacqueline Cooke**, N.T. Nunley, T. Willett-Gies, S. Zollner,* New Mexico State University

Using spectroscopic ellipsometry, we determined the dielectric function of LSAT, from the mid-IR to the deep UV (0.03 to 6.5 eV). LSAT is an acronym for the chemical formula $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.35}$, equivalent to $(La_{0.3}Sr_{0.7})(Al_{0.65}Ta_{0.35})O_3$. LSAT is a common substrate for epitaxial growth of complex metal oxides. Precise knowledge of the optical constants is useful to investigate the properties of epitaxial films grown on LSAT. We also investigated the band gap and the infrared-active phonons. Czochralski-grown LSAT wafers with (001) surface orientation were obtained commercially (MTI Corp., Richmond, CA). Single-side polished wafers were used for spectroscopic ellipsometry and two-side polished wafers with 0.5 mm thickness for transmission. Between 0.8 and 6.5 eV, we measured the normal-incidence transmission and the ellipsometric angles from 60° to 80° incidence in 2° steps on a J.A. Woollam variable angle of incidence ellipsometer with a computer-controlled Berek waveplate compensator. We also measured in the mid-IR on a rotating compensator FTIR ellipsometer. Transmission measurements show a steep rise of the absorption coefficient (α) between 4.6 and 4.8 eV, where LSAT becomes opaque. Fitting the ellipsometry data with a model containing two Tauc-Lorentz oscillators and 19 Å surface roughness thickness yields an excellent fit to the data. The Tauc gap is 4.9 eV and the high-frequency dielectric constant ε_∞= 4.0. Plotting α^2 versus photon energy yields a direct band gap of 5.8 eV. An Urbach tail extends towards lower energies. The resulting dielectric function is in agreement with previous ellipsometry and minimum-deviation prism measurements. The mid-IR dielectric function shows four ε_2 peaks due to TO phonon absorption. The loss function shows four LO peaks. A fifth TO phonon was seen at 155 cm^{-1} in far-IR ellipsometry. An ideal ABO3 perovskite has only three IR-active TO phonons. FCC ordering on the B-site as in (Sr_2AlTaO_3) adds a fourth phonon. We argue that the TO phonons at 155 and 283 cm^{-1} are vibrations of the tetrahedra against the La/Sr sublattices, respectively (mode splitting due to disorder). On the other hand, the 397 and 442 cm^{-1} modes are B-O bending modes due ordering in the Al/Ta sublattice. Finally, a B-O stretch mode at 664 cm^{-1} and broad two-phonon absorption at 765 cm^{-1} are also found. Fitting the spectra with a factorized TO/LO model yields better results than a sum of Lorentzians, because the individual TO/LO pairs are not well separated. The presence of FCC ordering was also confirmed with x-ray diffraction. We will also discuss temperature dependent ellipsometry and transmission measurements.

10:00am **EL+AS+EM+MI+TF-FrM6 A New Constant of Product of Electronic Scattering Time and Resistivity in Thin Silver Refractive Index Calculation from Ellipsometry and Resistivity Measurements***, **Guowen Ding**, C. Clavero, D. Schweigert, M. Le,* Intermolecular, Inc.

The optical and electrical response of metal thin films is highly affected by electronic scattering with the interfaces and defects. We are able to successfully model the electrical resistivity and near infrared (IR) optical response using a thickness dependent electronic scattering time. We investigated Ag films thickness in the range of 3 nm to 74 nm and determined that the product of electronic scattering time (τ) and resistivity (ρ) remains constant regardless of the thickness ($\tau \times \rho = C$), with a value of 59±2 μΩ cm·fs for Ag films. As a result, determining the constant C for a given thin film will allow to calculate the propreties of the film over a large range of wavelengths while limiting the number of measurements.Our findings enable us to develop a theoretical framework to determine the optical response of metal thin films in the near IR by using single wavelength ellipsometer measurements. An excellent agreement is found between experimental measurements and predicted values. We first reported this constant $\tau \times \rho =C$ for silver, and we posit that such constant concept could be applied for other conducting films. Application of the model presented here will allow rapid characterization of the IR optical response of metal thin films, with important application in a broad spectrum of fundamental and industrial applications, including optical coatings, low-emissivity windows and semiconductor industry.

10:20am **EL+AS+EM+MI+TF-FrM7 Realization of an *In Situ* Mueller-matrix Imaging Ellipsometer for the Real Time Observation of Surface Properties in an Ultra-high Vacuum EUV Facility***, **Pim Muilwijk**, N.B. Koster, F.T. Molkenboer, E. Sligte, te, A.F. Deutz, P. Walle, van der,* TNO Technical Sciences, Netherlands

TNO is realizing EUV Beamline 2 (EBL2), a facility to investigate the effects of Extreme Ultra-Violet (EUV) radiation on surfaces to enable future EUV High Volume Manufacturing (HVM) production. In this facility, samples with sizes up to 152x152x20 mm (6” EUV reticles) can be exposed to EUV radiation of up to 500W equivalent at intermediate focus (IF) under realistic environmental conditions and analyzed by in-situ ellipsometry and XPS. EBL2 consists of EUV source, automated handling system, beam line and an exposure chamber with an in-situ dual wavelength Mueller-matrix imaging ellipsometer.

Light from the dual wavelength light source (405 & 640nm) enters the exposure chamber through a polarizer, configurable retarder and a vacuum window producing a defined polarization state. After reflecting off of the sample, the light exits the exposure chamber through a vacuum window, configurable retarder and polarizer. The sample position is imaged on two camera’s, one for each wavelength. By combining all combinations of 4 polarization illumination states with 4 analyser states the full Mueller matrix of the sample can be recovered.

Calibration is performed in-situ with two insertable polarizers and two different calibration samples. The calibration procedure does not require prior knowledge of the polarizer orientation nor of the calibration samples.

This presentation will focus on the design and realization of the ellipsometer and will also touch upon the process of interpreting the data.

EBL2 will be publicly accessible as a test facility for EUV lithography related research after qualification, which is expected to be finished end of Q1 2017.

10:40am **EL+AS+EM+MI+TF-FrM8 Conducting, Semi-Conducting and Insulating 2D-Materials Characterized by Spectroscopic Imaging Ellipsometry***, **Matthias Duwe**, S. Funke,* Accurion GmbH, Germany*; U. Wurstbauer,* Technical University of Munich, Germany*; A. Matkovic,* University of Belgrade, Serbia*; A. Green,* SUNY College of Nanoscale Science and Engineering*; A. Molina-Mendoza,* Universidad Autonoma de Madrid, Spain*; A. Castellanos-Gomez,* IMDEA Nanoscience, Spain*; P.H. Thiesen,* Accurion GmbH, Germany

Finding thin-film flakes of 2D-materials after the fabrication and identifying their layer thicknesses often is a challenging and time-consuming task. Here, we present various applications of spectroscopic imaging ellipsometry (SIE) to a variety of conducting, semi-conducting, and insulating 2D-Materials such as graphene, molybdenum disulfide (MoS_2), hexagonal boron nitride, and black phosphorus. As a combination of polarization-contrast microscopy and spectroscopic ellipsometry, SIE measurements localize microscopic flakes of the 2D-materials, yield the samples’ optical dispersion functions, and determine the layer thicknesses.

Matkovic et al. [1] characterized monolayers of graphene by SIE, and they obtained the optical dispersion by Fano-resonance modelling. Using this dispersion, SIE offers a straightforward search for and identification of few-layer graphene flakes on various opaque or transparent substrates. As this flake search uses ellipsometric measurements, it depends far less on the used substrate compared to e.g. conventional light-microscopy. In a similar procedure, SIE identified monolayers of insulating hexagonal boron nitride, and it yielded the material‘s optical properties.

SIE measurements on MoS_2 revealed the repercussion of the used substrate [2]. Ellipsometric contrast micrographs showed the lateral variation of the optical parameters for a structured flake. Spectroscopic measurements of the ellipsometric values (Ψ & Δ) obtained from selected regions of interest on the flake yielded the optical dispersion for the in-plane and out-of-plane components of the dielectric function in the visible spectral range.

Finally, we will present imaging Mueller-matrix ellipsometry (IMME) for the characterization of thin-film flakes of the semi-conducting 2D-material black phosphorus. In contrast to MoS_2, black phosphorus also features an optical in-plane anisotropy. IMME-micrographs easily reveal this anisotropy as the Mueller matrix's off-diagonal blocks deviate from zero. By performing spectroscopic Mueller-Matrix mapping and rotational Mueller-matrix measurements combined with atomic force microscopy, we obtained the flake’s layer thickness, the orientations of the optical axes, and the material's optical properties in the visible spectral range.

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