Actinides and Rare Earths Focus Topic

Room: 301 - Session AC+AS+MI+SA+SS-MoM

Spectroscopy, Microscopy and Dichroism of Actinides and Rare Earths

Moderator: David Shuh, Lawrence Berkeley National Laboratory


The development of a detailed, quantitative understanding of electronic structure and bonding for a broad range actinide materials remains a significant scientific challenge. Recent advances have shown that the 1s to np transition intensities measured by Cl and S K-edge X-ray absorption spectroscopy (XAS) directly relate to coefficients of covalent orbital mixing and quantified covalency for ligands beyond Cl and S would have a wide impact. The nature of chemical bonds between actinides and light atoms such as oxygen, nitrogen, and carbon is of particular interest because these interactions control the physics and chemistry of many technologically important processes in nuclear science. However, obtaining accurate light atom K-edge XAS spectra on non-conducting compounds is notoriously difficult, because the measurement is highly sensitive to surface contamination, self-absorption, and saturation effects. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Specifically, comparing XAS spectra measured in transmission with a scanning transmission X-ray microscope (STXM) with those from non-resonant inelastic X-ray scattering (NIXS) and time-dependent density functional theory provides a sound basis for validation of bulk-like excitation spectra.

Herein, a new effort is discussed that employs these techniques to understand bonding interactions in two well defined series of f-element materials. The actinide sandwich complexes, “actinocenes,” (C₈H₈)₂An (An = Th, Pa, U, Np, Pu) have played a central role in the development of organoactinide chemistry. Results showed two contrasting trends in actinocenes and XAS studies suggests that using synchrotron-generated radiation to quantify covalency for ligands beyond Cl and S would have a wide impact. The nature of chemical bonds between actinides and light atoms such as oxygen, nitrogen, and carbon is of particular interest because these interactions control the physics and chemistry of many technologically important processes in nuclear science. However, obtaining accurate light atom K-edge XAS spectra on non-conducting compounds is notoriously difficult, because the measurement is highly sensitive to surface contamination, self-absorption, and saturation effects. Fortunately, recent upgrades at synchrotron facilities, advancements in beamline instrumentation, and sample preparation methods suggest that these insights are now within reach. Specifically, comparing XAS spectra measured in transmission with a scanning transmission X-ray microscope (STXM) with those from non-resonant inelastic X-ray scattering (NIXS) and time-dependent density functional theory provides a sound basis for validation of bulk-like excitation spectra.

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9:00am AC+AS+MI+SA+SS-MoM3 X-ray Magnetic Circular Dichroism of Actinides, Andrei Rogalev, F. Wilhelm, European Synchrotron Radiation Facility (ESRF), France

X-ray Magnetic Circular Dichroism (XMCD) is an established experimental probe of atomic-specific magnetic properties of lanthanides and actinides. In XMCD, a photon of well-defined energy and polarization is absorbed by an atom in the sample with a probability that is proportional to the number of available unoccupied states with an energy that allows fulfilling the energy conservation and selection rules. An essential element of XMCD are so called sum rules [2,3], which relate the XMCD spectra to the spin and orbital angular momenta, respectively.

Recently, a new experimental method has been developed that is closely related to XMCD. It was named electron magnetic circular (or chiral) dichroism (EMCD) and it is measured with a transmission electron microscope (TEM) instead of a synchrotron beam-line. We will review the short history of this method starting from its proposal in 2003 [4], first experimental proof-of-the-concept in 2006 [5], formulation of the theory [6] and sum rules [7,8] in 2007 to the present state-of-the-art and early applications, for example [9-12]. Yet, despite intense efforts, EMCD is still in its development phase, particularly from the point of view of quantitative studies. On the other hand, qualitative EMCD experiments have reached resolutions below 2nm [13].

The primary advantages of the EMCD, when compared to XMCD, are costs, availability and lateral resolution. Even a state-of-the-art TEM is a device considerably cheaper than a synchrotron beam-line and as such it can be available locally to a research group. TEM is also a very versatile instrument that combines diffraction experiments, elemental analysis, local electronic structure studies via electron energy loss spectroscopy [14] and now also magnetism via EMCD.

The Microstructure of Plutonium Hydride Growth Sites, Martin Brierley, J.P. Knowles, AWE, UK, M. Press, A.H. Sherry, University of Manchester, UK

Under certain conditions plutonium is able to form plutonium hydride during long term storage [1]. Plutonium is radioactive, decaying via release of an alpha particle. Alpha particles are particularly damaging within the body and every attempt should be made to limit the distribution of loose material. Plutonium hydrides have been shown to be pyrophoric when exposed to air. Such a reaction could potentially liberate loose particulate outside of suitable containment.

Previous work into the hydriding rate of plutonium has investigated the reaction rate of various hydrides on the surface of these materials; specifically the nucleation rate, the lateral growth rate and the specific hydriding rate [2, 3]. Plutonium is a reactive metal and quickly forms a semi-protective oxide layer in air. Upon exposure of an oxide-covered sample to hydrogen, hydride is formed at discrete sites on the surface, which then grow outwards across the surface [1]. Recent work has suggested a grain boundary enhanced growth rate [4].

In the present study, the microstructure associated with selected plutonium hydride growth sites was studied to provide information regarding the nucleation and growth mechanisms that govern the formation of plutonium-hydride. The samples were ground to 600 grit and evacuated before being exposed to ultra-pure hydrogen at pressures between 10 mbar and 1000 mbar for sufficient time to have nucleated a number of hydride sites. Post-test analysis was performed using Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) to determine the microstructure of the hydride growth sites. The morphology of individual hydride growth sites indicates that the hydride-metal interface has a highly discontinuous boundary, resulting from enhanced grain boundary diffusion and spears of transformed material; the microstructure within the plutonium hydride growth sites indicates that a preferred growth habit was adopted by the hydride product.

References

11:00am AC+AS+S+M+SS-MoM9 Hydrides of U-Mo and U-Zr Alloys: Structure and Electronic Properties, Ladislav Havela, M. Paulovic, I. Tkach, D. Drozdenco, M. Cieslar, Z. Matej, Charles University, Czech Republic

When U metal (α-U) is exposed to H gas, it forms a stable hydride β-UH2. The lattice expansion stabilizes the ferromagnetic order with the Curie temperature around 170 K. The metastable form, β′-UH2, has been shown to be pyrophoric when exposed to air. Such a reaction could potentially liberate loose particulate outside of suitable containment.

New class of U materials, which exhibit, irrespective of details of synthesis for materials at which the inter-atomic spacing does not exceed appreciably the Hill limit 340-360 pm. At last, the variations using double doping (both Mo and Zr) will be presented.

References
Because of the technological relevance of the Si [001] surface, the Si 2p is one of the most studied core levels with laboratory X-Ray Photoelectron Spectroscopy (XPS). An important application is the quantification of the thickness of oxide layer, which is done by comparing the intensity of the substrate and Si$^{4+}$ components. Peak-fitting is usually done by employing one doublet for the substrate and another for the Si$^{4+}$ shifted around 3.5 or 4 eV to higher binding energy (from the substrate). In detailed studies, the quantification of the suboxides is usually done employing components, originally proposed by Himpel et al., with the following shifts: 2.5 eV for Si$^{3+}$, 1.75 eV for Si$^{2+}$, and 0.95 eV for Si$^{1+}$. A proper fit, besides those five components, actually requires a six component shifted by approximately 0.3 eV. This peak has been clearly identified in various synchrotron studies such as that by Landemark et al., where it is referred as $S'$. In that study, and in others, it is assigned to one monolayer (the second) of the substrate.

Although clearly present in Si 2p spectra obtained with laboratory XPS equipped with monochromatized Al Kα radiation, this component is largely unspoken in the literature. In one of the few studies that mention its existence it is assigned to an anomaly of the bulk peak. In this presentation it is going to be shown that this interpretation is inconsistent with the angular dependence observed by the authors. The physical origin of $S'$, which is going to be discussed in detail, goes in a direction compatible with that proposed by Landemark et al.: although it represents one monolayer for the clean Si [001] surface, for oxide-covered surfaces it corresponds to a few monolayers of the substrate.


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

**Theory**

The theoretical approach to signal emission in electron spectroscopy is discussed on the basis of so-called Landau-Goudesmit-Saunderson (LGS) loss function, which leads in a natural way to rigorous spectrum analysis techniques, the so-called partial intensity analysis (PIA). Examples of application include theoretical calculation of model spectra as well as analysis of experimental spectra using of X-ray Photoelectron Spectroscopy (XPS) and Reflection Electron Energy Loss Spectroscopy on nanostructured surfaces. The contribution of inelastic electron scattering to electron spectra 


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

**Angle-Resolved XPS**

Non-destructive depth-profiling by inversion of Angle Resolved XPS spectra has been a desire in the XPS community for a long time. The lack of reference specimens with known structures has been a severe handicap in the development of the technique. Until now, reference materials with known depth-profiles have largely been confined to thin oxide layers on aluminium or silicon, and even these have uncertain carbon contamination layers. Progress has been made, though, with depth-profiling numerical methods that need comparison with real known structures. It is difficult to fabricate structures with nanometre-scale variation in concentration without even more difficult to transport them without contamination (and the potentially damaging removal of such contamination). We have developed protocols for the fabrication of two different samples, one organic and the other inorganic, with known depth-profiles in situ in XPS instruments.

**Glancing-angle monatomic argon sputtered PEDOT:PSS, a common conducting polymer blend, and Argon cluster-ion sputtered indium arsenide (InAs), a compound semiconductor**

Indium arsenide and PEDOT:PSS are both widely-available, almost atomically flat and sufficiently electrically conductive to ensure no sample charging occurs. Glancing angle monatomic sputtering of PEDOT:PSS leaves a PEDOT enhanced region at the surface, the spatial parameters of which depend only on sputtering ion conditions under direct experimental control. Recently we have demonstrated the unexpected result that argon gas-cluster sputtering of InAs results in a thin, coherent metallic indium layer at the surface, the basis for InAs reference material structure. The ill-posed nature of the inversion of ARXPS data means it is sensitive to small experimental uncertainties. We apply three different ARXPS algorithms, including regularization, to the data from these in situ reference structures. This gives a set of reference data that will allow comparison with results from any XPS works following the same sample preparation. This should greatly improve confidence in the results of ARXPS depth-profiling.

embracing both experimental and theoretical determinations at any level of uncertainty in any field of science and technology." Besides the establishment of full uncertainty budgets traceability is another aspect of metrology.

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

1. Primary methods measuring amount of substance as \[ \text{[atoms/cm}^2, \ldots \] 
2. Empirical methods measuring amount of substance after calibration as fractions of a nano scaled surface layer
3. Primary and empirical methods measuring amount of substance expressed as the thickness of a thin film [nm]

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

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

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

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

Progress in high-resolution real space imaging techniques such as (Scanning) Transmission Electron Microscopy (STEM) and Scanning Tunneling Microscopy (STM) has allowed high veracity, direct imaging of atomic columns (STEM) and surface atomic structures. While the data acquisition platforms are continuously evolving, the basic data processing principle - analysis of structure factor, or equivalently two point correlation function averaged over probing volume – remained invariant since the early days of Bragg's. We propose an approach based on the multivariate statistical analysis of the coordination spheres of individual atoms to reveal preferential structures and symmetries. The underlying mechanism is that for each atom, \( i \), laying on the lattice site with indices \( (l, m) \), we construct a near coordination sphere as a vector \( N_i \equiv (s_{i1}, s_{i2}) \), where \( s_{ij} \) is the radii dius vector to \( j \)-th nearest neighbor. Once the set of \( N \) vectors is assembled, its statistical properties are analyzed though cluster analysis and various multivariate methods to reveal and extract regions of symmetry, distortions, different phases, boundaries, defects, etc. Results are presented on various model and real material systems including \( \text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3 \), \( \text{Fe}_2\text{O}_3 \), \( \text{CoFe}_2\text{O}_4 \) and discussed in light of physical parameter extraction.

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11:20am AS+MC-MoM10 Chemical Warfare Agent Surface Adsorption: Hydrogen Bonding of Sarin and Soman to Amorphous Silica. Erin Durke, W.O. Gordon, Edgewood Chemical Biological Center, A.R. Wheatley, Augustana College. D. Tova, J.R. Morris, Virginia Tech Sarin and soman are warfare nerve agents that represent some of the most toxic compounds ever synthesized. The extreme risk in handling such molecules has, until now, precluded detailed research into the surface chemistry of agents. We have developed a surface science approach to explore the fundamental nature of hydrogen bonding forces between these agents and a hydroxylated surface. Sarin and soman are deposited via a directed dosing technique on an amorphous silica support and characterized by reflection-absorption infrared spectroscopy (RAIRS) in an ultra-high vacuum (UHV) chamber. Once the chemical agent coverage reached monolayer values, temperature programmed desorption is performed to determine the binding energy. Changes in the OH region of the IR spectra are monitored in real time with RAIRS, and the degree of shift in the H-bonded OH peak shows a linear relationship with the strength of the interaction between agent and silica surface. Infrared spectroscopy revealed that both agents adsorb to amorphous silica through the formation of surprisingly strong hydrogen-bonding interactions with primarily isolated silanol groups (SiOH). Comparisons with previous theoretical results reveal that this bonding occurs almost exclusively through the phosphoryl oxygen (P=O) of the agent. Temperature-programmed desorption experiments determined that the activation energy for hydrogen bond rupture and desorption of sarin and soman was 50 ± 2 kJ/mol and 52 ± 2 kJ/mol, respectively. X-ray photoelectron spectroscopy (XPS) is also used to confirm molecular desorption of the agents from the silica substrate. Together with results from previous studies involving other phosphoryl-containing molecules, we have constructed a detailed understanding of the structure-function relationship for nerve agent hydrogen bonding at the gas-surface interface.
gradient. Experimentally, a configuration with four furnaces in line has been constructed which allows the inner wall of a tube 12" in length and 1/8" inner diameter to be coated with a layer of even thickness, with a prominent application being the partial protection of thin silver layers which are deposited on the inner walls of catheters of polyurethane or polysilicone not as a contiguous film but with a zebra-stripe design applying a patented procedure [1]. First results for the CVD of polyarylene are presented and are discussed and modeled with COMSOL in terms of diffusion laws with an abstraction reaction and a reaction order. After having shown the antibacterial effect for a static case [4], here a dynamic trial is presented to simulate the antibacterial activity during flow of bacteria-containing urine in the ureters. [1] G. Franz, F. Schamberger, A. Kutschera, S. Seyedi, D. Jocham, German patent disclosure DE 102012023349.3, Nov. 29, 2012, [2] F. Schamberger, A. Ziegler, and G. Franz, J. Vac. Sci. Technol. B30, 018102 (2012) [3] G. Franz, F. Schamberger, J. Vac. Sci. Technol. A31, 061602 (2013) [4] H. Heidari, St. Sudhop, F. Schamberger, G. Franz, Biointerphases, accepted May 05, 2014

9:00am BI+AS-MoM3 Deciphering the Scaling of Single Molecule Acid-Amine Interactions using Jarzynski’s Equality, S. Raman, T. Utzig, T. Bainpos, B.R. Shrestha, Markus Valtiner, Max Planck Institut für Eisenforschung GmbH, Germany

Unraveling the complexities of the macroscopic world based on molecular level studies relies on understanding the scaling of single molecular interactions towards integral interactions, which are mediated through a large number of simultaneously interacting molecular bonds. Here we demonstrate how to decipher the scaling of acid-amine interactions from the single molecular level towards the macroscopic level through a synergistic experimental approach combining equilibrium Surface Forces Apparatus (SFA) experiments and nonequilibrium single molecule force spectroscopy (SM-AMF). Combining these two techniques is ideally suited for testing the largely praised Jarzynski’s equality (JE), which relates the work performed under non-equilibrium conditions with the equilibrium free energy. Large-scale equilibrium force measurements using SFA scale linearly with the number density of acid-base bond at an interface and we measure non-equilibrium single molecule interaction energies of 10.9 ± 0.2 kT. AFM single molecule experiments reveal two distinct regimes. As expected, far from equilibrium the measured single molecule unbinding forces increase exponentially with the loading rate. A second quasi-equilibrium regime at loading rates close to and below the natural binding/unbinding rate of the acid-amine bond shows little loading rate dependence. Irrespective of how far from equilibrium AFM experiments are performed, the energy calculation using the JE aligns well with HAP surface forces. This result is experimentally equivalent to the value measured by the equilibrium measurements using SFA. Our results suggest that using Jarzynski’s equality allows direct scaling of non-equilibrium single molecule interaction force measurements to scenarios where a large number of molecules are simultaneously interacting, giving rise to macroscopic equilibrated interaction energies. Taken together, this approach opens a new strategy for modeling and designing molecular interactions at the single molecular level towards the macroscopic level through a synergistic approach combining equilibrium and nonequilibrium single molecule force spectroscopy.

9:20am BI+AS-MoM4 Fabrication of ssDNA Monolayers, Custom Designed ssDNA Arrays and Brush Patterns in Bioresponsive Templates by Promoted Exchange Reaction, M.N. Khan, University of Heidelberg, Germany, Y. Tsubouchi, Chikato, Duke University, Michael Zhanrownik, University of Heidelberg, Germany

We present here a versatile approach to prepare mixed monolayers of thiolate-bound single stranded DNA (ssDNA) and oligo(ethylene glycol) substituted alkaneethiols (OEG-AT) in a broad range of compositions as well as ssDNA/OEG-AT patterns of desired shape embedded into a bioresponsive background. The procedure involves two steps. First, a OEG-AT monolayer on gold is assembled by exposure to a layer of even thickness, either homogeneous or lithographic fashion. Second, the promoted (by ultraviolet light) exchange reaction between the damaged OEG-AT species in the film and ssDNA substrates in solution occurs, resulting in formation of a ssDNA/OEG-AT monolayer or pattern. The composition of the mixed films or ssDNA/OEG-AT spots (lithography) can be precisely adjusted by an electron or UV light dose in an almost compositional range. The above procedure relies on commercially available compounds and is applicable to both thiol-terminated and symmetric and asymmetric disulfide-terminated ssDNA. The fabricated OEG-AT/ssDNA templates and patterns can be extended into the z-dimension by surface-initiated enzymatic polymerization of ssDNA, which results in the formation of highly ordered ssDNA brushes and allows topographically complex ssDNA brush patterns to be sculpted on the surface.

9:40am BI+AS-MoM5 High Throughput BioMaterials Screening using Microarrays and High Information Content Imaging Methods, S. Boudjidi, D. Covelli, M. Keramane, E. Luckham, John Brennan, McMaster University, Canada

This presentation will highlight recent work in the area of high throughput screening of biologically modified surfaces for production of biosensors, proteins, and cell microarrays. The presented array provides a robotic material synthesis and assay systems and a combination of contact and contactless microarray printing, we have produced several libraries of biomaterials with a wide range of chemical compositions based on acrylate, silicone and silicon-based polymers. Using silica-based materials as an example, the presentation will show the workflow utilized to develop new bioactive polymer materials for further fabrication and sealing of microfluidic devices and coatings. This includes methods to produce several thousand materials very rapidly via printing, rapid imaging tools and assays for screening to identify “hits” that show a desired property (i.e., high bioactivity, low nonspecific binding), and methods for detailed material analysis using a range of imaging methods based on fluorescence, XPS, MALDI-MS/MS, FTIR and SPR to fully characterize the properties of biologically active materials. Methods for mining and analyzing the large datasets produced using our in-house developed Biointerfaces Research Gateway will be described.

10:40am BI+AS-MoM8 Osteocalcin Adsorption onto Calcium Phosphate and Silica Surfaces, L.A. Scudeller, David Castner, University of Washington

Osteocalcin (OC) is the most abundant, non-collagenous protein in bone and accounts for almost 2% of total protein in the human body. OC plays a role in regulating the metabolism and function of bone cell, as well as being used as a biocompatible chemical for bone formation. However, its precise function is not known. OC is known to bind strongly to hydroxyapatite (HAP). This strong binding is likely the result of the γ-carboxylated glutamic acid residues (Gla) in OC interacting with Ca2+ ions on the HAP surface. OC has three helical units (α-1, α-2 and α-3) and the spacing of the 3 Gla residues in the α-1 unit match well the lattice spacing of the (001) HAP surface.

This study uses x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate the adsorption of OC and decarboxylated (i.e., Gla converted back to Glu) OC (dOC) onto various calcium phosphate surfaces as well as silica surfaces. The XPS nitrogen signal is used to track the amount of adsorbed OC and dOC. The intensities of key ToF-SIMS amino acid fragments are used to assess changes in the structure of adsorbed OC and dOC.

The largest differences were observed between OC and dOC adsorbed onto the hydroxyapatite surfaces (~30% decrease). For OC and dOC adsorption onto the silica surface, no significant changes were observed. The highest amount of adsorbed OC (~10% atomic % for dOC and ~8% atomic % for OC). The ToF-SIMS data showed the intensity of the Cys amino acid fragment, normalized to intensity of all amino acid fragments, was significantly higher (~10) when the proteins were adsorbed onto silica. Since in the native OC structure the cysteine residues are buried in the center of the 3 α-helices, this indicates both OC and dOC are more denatured on the silica surface. As OC and dOC denature upon adsorption to the silica surface the cysteines become more exposed and are more readily detected by ToF-SIMS. No significant differences were detected between OC and dOC adsorbed onto the silica surface, but small differences were observed between OC and dOC adsorbed onto the HAP surface. In the OC structure the α-3 helix is located on the α-1 and α-2 helices. Small differences in the ToF-SIMS intensities from amino acid fragments characteristic of each helical unit (Asn for α-1; His for α-2; and Phe for α-3) suggests either slight changes in the orientation or a slight uncovering of the α-1 and α-2 for adsorbed dOC.

XPS showed similar amounts of OC and dOC were adsorbed onto amorphous HAP, crystalline HAP and octacalcium phosphate, but ToF-SIMS detected some small differences in the amino acid fragment intensities between adsorbed OC and dOC.

11:00am BI+AS-MoM9 Reversible Activation of a pH-sensitive Cell Penetrating Peptides Attached to Gold Surfaces, Joe Bia, Oregon State University, D. Schuch, University of Chicago, M. Bonn, T. Weidner, Max Planck Institute for Polymer Research, Germany

GALA peptides (WEAALAEALAEALAEALAEALAEALAA) mimic pH-sensitive viral fusion proteins and are widely touted as a promising route to achieve site-specific delivery of therapeutic compounds. At basic pH, GALA assumes a random coil structure but when lowering the pH to acidic conditions the peptide transitions into an alpha helical structure. In this state, GALA has the ability to penetrate cell membranes and form
pores. This mechanism is mainly driven by the change in overall charge of the glutamic acid side chains. One development of GALA mediated drug delivery is the immobilization of these peptides onto Au nanoparticles. Here we demonstrate, using a variety of spectroscopic techniques, that GALA can self-assemble into a protein monolayer on a gold film, linked to the surface via a single cysteine synthesized to the carbonyl terminus. Transmission IR vibrational spectroscopy demonstrates that the addition of this cysteine does not impede the pH transition between a helix and random coil structure in solution. Detailed characterization of the thiol-Au immobilization scheme by X-ray photoelectron spectroscopy illustrates that this single cysteine induced the formation of a well-ordered protein monolayer. To directly observe any pH triggered transition of this protein monolayer, sum frequency generation (SFG) vibrational spectra, at the amide I vibrational band, were collected at four different pH environments. A vibration mode at 1655 cm⁻¹, related to a helical structure, appears when this monolayer is immersed in a buffer at acidic conditions (pH 3 and 5) and then disappears under basic conditions (pH 9 and 12). While the surface immobilization clearly reduces the effective glutamic acid pKa, from a bulk solution value of 6 to 5.5, the covalently bound GALA-cysteine monolayer reliably retained the reversible, pH-driven helix-coil transition mechanism. Our findings establish that covalent attachment of GALA via cysteine linkers is a promising route for drug delivery applications and the design of ‘smart’ biological coatings.

11:20am BI+AS-MoM10 Polypolyamine Modification Using Small Molecule Thiol and Dithiols: Problems and Solutions for Creating Protein Resistant Coatings, Marlon Walker, A. Vaish, D. Vanderah, National Institute of Standards and Technology (NIST) Polypolyamine (PDA) is emerging as an increasingly useful bio-inspired coating for surface modification. Generated by a condensation reaction of dopamine in aqueous media under alkaline conditions, it can be readily deposited on almost any surface, forming thin films of controllable thicknesses. One useful attribute of a PDA coating is that it can be placed on and further modified to exhibit desired properties not possible with the underlying substrate. We present results of functionalizing PDA-coated surfaces on substrates such as silicon with oligo (ethylene oxide) thiols and dithiols for non-specific protein adsorption resistance.

11:40am BI+AS-MoM11 A Process to Functionalize Polyaniline for Biotin-Avidin Biosensing, Tianha Shao, M.D. Williams, Clark Atlanta University Biotin-avidin technology is a widely explored interaction in bioscience. Biotin’s affinity for the protein avidin, makes it ideal for protein and nucleic acid detection or purification methods. This strong interaction is often used in pretargeting strategies for cancer treatment. In most cases a probe molecule (antibody) is connected to a marker molecule (fluorophore or polymer’s hydroxyl group was functionalized by Steglich esterification of biocarboxylic acid of biotin to further reaction and DMAP (4-N,N-dimethylaminopyridine) acts as the acyl transfer catalyst. The biotinylated polyaniline derivative was characterized using FT-IR spectroscopy, ¹H NMR spectroscopy, UV-Vis spectroscopy, and Scanning Electron Microscopy. Florencecence emission studies were also carried out with the avidin protein.

Monday Morning, November 10, 2014 6

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

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


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

Atomprobe tomography is able to provide composition analysis within very small volumes (a few nm³) with high sensitivity and accuracy and excellent spatial resolution. Hence this enables to observe dopant atom migration in 3D-devices, and through some data mining analysis, even cluster formation as precursors to strain relaxation towards growth (and strain relaxation) mediated by the confined volume (for instance relying on aspect ratio trapping). Atomprobe tomography, a complement to APT, can be used to image impurity atoms clustered around defects within the crystal. Routine application of APT is still hampered by localization problems, reconstruction artifacts due to inhomoogenous evaporation, local magnification effects, sensitivity due to the limited statistics, laser-tip interaction phenomena, etc.

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

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

9:00am MC+AP+AS-MoM3 Characterization of the Peridocity (Pitch) and Stress of Transistor Fin Structures using X-Ray Diffraction Reciprocal Space Mapping, Mainie Dibold, M. Medikonda, SUNY College of Nanoscience and Engineering, M. Worlington, Jordan Valley Semiconductors Inc

Cleanroom compatible, high resolution X-Ray diffraction systems are now capable of measuring the average pitch and critical dimensions of ordered arrays of fins and the stress state of high mobility layers at the top of the fins. Reciprocal Space Mapping (RSM) characterizes both the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity. The periodicity of the fin arrays has decreased to the point where the fin array adds satellite diffraction peaks to the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity. The periodicity of the fin arrays has decreased to the point where the fin array adds satellite diffraction peaks to the main Bragg diffraction peak and the satellite peaks associated with the fin periodicity.

State of the art lithographic processing using the spacer patterning process often results in a different spacing between every other fin. This is known as pitch walking. Pitch walking is very difficult to observed, even using TEM cross-sectional images. The stress state of the high mobility epitaxial layers such as Si, Ge, on Si FinFETs can be characterized using RSMs. In addition, some of the higher order satellite peaks will split when the fins have a near rectangular shape. This presentation compares the capability of cleanroom and synchrotron based
XRD systems for reciprocal space mapping of Si and Si$_x$Ge$_{1-x}$/Si transistor fins arrays.  


By using compositionally graded buffer layers, InAsSb can be grown by molecular beam epitaxy with its inherent lattice properties across the entire composition range. This direct bandgap, III-V alloy of great interest for infrared detector applications, as it can cover both the mid (3-5 μm) and long wavelength (8-12 μm) bands. The direct bandgap provides the high quantum efficiency that allows it to directly compete with HgCdTe and for potentially much reduced fabrication costs. InAsSb was sidelined for decades, because conventional wisdom indicated its bandgap bowing parameter would not allow it to reach the needed 10-12 μm benchmark. The material was further maligned because it was thought to exhibit CuPt ordering, which affects the bandgap. By revisiting the growth techniques we have determined that the bandgap bowing parameter of InAsSb is more than sufficient for LWIR applications and it can be grown free of ordering, provided that the material is grown with its inherent, undistorted lattice constant. As there is no perfect substrate available for the InAsSb compositions of interest (typically containing ~40-50% Sb), we grow the films on compositionally graded buffer layers on GaSb substrates. The buffer layers consist of AlGaSb/GaSb, GaAsSb, or InAsSb grades based on the theories described in J. Tersoff. In this paper we provide experimental verification of Tersoff’s theories applied to ternary and quaternary grades, and for both tensile and compressive grades. Furthermore, the specific parameters calculated by Tersoff, such as the boundary for the dislocation-free region (Zc) is exactly verified by transmission electron microscopy (TEM).

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

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

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

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

Resistive switching has been observed in a multitude of inorganic (oxides, chalcogenides...) and hybrid (organic or polymers plus metal nanoparticles) thin films, and may be simply switched between two electrical states. These memory devices are particularly promising candidates for developing large scale, high density, cost efficient, non-volatile resistive memories. Their capability) and Time-of-Flight Secondary Ion Mass Spectrometry (for its quantitative information, with high depth resolution, is obtained for the heavier elements between silver and indium tin oxide electrodes. Depth profiles evidence the metal diffusion in pristine and electrically addressed memory elements throughout the whole organic thin film, where the silver concentration can reach a value as high as 5.10$^{19}$ at/cm$^3$. Filament formation is shown to be initiated during the top electrode evaporation, and is then successively enhanced by field induced diffusion during the electrical addressing. The 3-D ToF-SIMS images evidenced the formation of metallic paths extending through the entire device depth, electrically bridging the two electrodes when the element is in its low resistance state. Filaments with different metallic phases have also been studied in organic memories based on a semiconducting polymer (Polymer Ni1400 ActiveInk) or on semiconducting small molecules (Tris-(8-hydroxyquinoline)aluminum, Alq). It appears therefore that metallic filaments are indeed at the origin of switching in organic memory devices.


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


INVITED Modern day technologies are increasingly based on high performance nanomaterials and novel preparation techniques for such materials are developed at a rapid pace. Advances in nanoscience and nanotechnology heavily rely on the availability of analytic techniques that can validate and support new nanomaterials synthesis procedures. With the introducing of the Qte$$^{[9]}$$, a new high-sensitivity Low Energy Ion Scattering (HS-LEIS) instrument, one can quantitatively analyze the atomic composition of the surface of a wide range of materials with an unparalleled surface sensitive capability to the outermost atoms of a surface largely control processes such as growth, nucleation, poisoning, adhesion and electron emission. While analytic tools (such as XPS) probe an average of many atomic layers, LEIS can selectively analyze the outer atoms. In addition, non-destructive in-depth information, with high depth resolution, is obtained for the heavier elements (0 - 10 nm). HS-LEIS is just as well suited for the quantitative analysis of amorphous, insulating and extremely rough surfaces as for flat single crystals. Since HS-LEIS is a fast analysis technique, it can be used to follow diffusion processes in-situ.

The focus will be on applications where valuable information has been obtained that is impossible (or very difficult) to obtain with other analytic techniques. The unique possibilities will be illustrated with state-of-the-art applications for: ALD growth of ultra-thin layers, surface modification, interface diffusion, core/shell nanoparticles, graphene, self-assembled monolayers for sensors.
Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed were proposed. band diagrams of these MFIS devices during program and erase operations properties were achieved due to the presence of BTBCN. The electronic applied voltage of -1 V. The wide memory window and superior retention, as charge storing elements was also established. The X-ray diffraction and clearly demonstrate the single crystallization of BTBCN ferroelectric films. In particular, Auger depth profiling performed on HfO2/TiAl/TiAl/W gate stacks at low energy (500 eV Ar+) brought the following main conclusions: a) no Al diffusion toward the HfO2/TiAl interface, b) nitrogen out diffusion in the upper TiAl film, c) significant oxygen scavenging. By comparison, these results evidenced that Auger frontside analyses suffer from sputter-induced artifacts.

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

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


11:40am MC+A+P+AS-MoM11 Charge Storage Properties of Al(1-x)BaTiO3-xBa(Cu1/3Nb2/3)O3 (x = 0.025) [BTBCN]/HfO2/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices, Souvik Kundu, Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed laser deposited 300 nm (1-x)BaTiO3-xBaCu(1/3)Nb(2/3)O3 (x = 0.025) (BTBCN)/HfO2/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices. Sowvik Kundu, Metal-ferroelectric-insulator-semiconductor (MFIS) devices with pulsed laser deposited 300 nm (1-x)BaTiO3-xBaCu(1/3)Nb(2/3)O3 (x = 0.025) (BTBCN)/HfO2/p-Si Metal/Ferroelectric/Insulator/Semiconductor Devices.

The leakage current of these devices was found to be 7×10^-7 A/cm² at an applied voltage of -1 V. The wide memory window and superior retention properties were achieved due to the presence of BTBCN. The electronic band diagrams of these MFIS devices during program and erase operations were proposed.
9:20am SS+AS+EN-MoM4 The Co-adsorption of Water and ammonia on Pt(111), B.A.J. Lechner, Lawrence Berkeley National Laboratory. Y. Kim, H. Kang, Yonsei National University, Korea, Miguel Salmeron, Lawrence Berkeley National Laboratory

Water (H2O) and ammonia (NH3) are arguably the most important inorganic molecules in the chemical industry. Both have the ability to form hydrogen bonds and mix readily in the liquid form. However, upon adsorption onto a metal surface, the molecules can form fewer yet more directional hydrogen bonds. To investigate the interaction between these two species at the molecular level we present a scanning tunneling microscopy (STM) study of the co-adsorption of water and ammonia on Pt(111), a substrate which bonds both molecules strongly but does not promote their decomposition.

Prior investigations have suggested the formation of the ammonium ion, NH4+, upon adsorption of ammonia onto a water monolayer on Ru(0001) [1], implying that the two molecules react readily when adsorbed on transition metal surfaces. Furthermore, a theoretical study of the co-adsorption of ammonia and water on Cu(110) proposed an intimately mixed layer of ammonia and water as the energetically most favorable structure [2].

Here, we present the first microscopic investigation of co-adsorbed water and ammonia species. Upon adsorption at 4 K, ammonia and water form disordered structures, yet as the temperature is increased the two species segregate on the substrate. Indeed, at temperatures above 77 K, ammonia invariably prefers to bond to the Pt surface and only adsorbs on a water film once the monolayer is complete and no active sites remain on the substrate. When adsorbed on the water layer, we find that ammonia bonds to the water molecules that are lifted off the substrate due to a lattice mismatch of the water monolayer and the Pt(111) geometry, which we believe is due to their ability to provide a hydrogen atom for the hydrogen bond more readily than the molecules bonded more strongly to the substrate.


9:40am SS+AS+EN-MoM5 Thermal Decomposition of Ethylene on Ru(001), Yuan Ren, I. Walyuo, M. Trenary, University of Illinois at Chicago

Ruthenium is an important catalyst in the Fischer-Tropsch process which deals with the conversion of syngas (CO and H2) into hydrocarbons. One of the most important aspects in the Fischer-Tropsch reaction is the chain growth from a C1 species to longer chain hydrocarbons. It is, therefore, important to study the chemistry of various CnHx hydrocarbon fragments on transition metal surfaces as building blocks in the chain growth mechanism. Ethylidyne (CCHx) is an interesting hydrocarbon fragment that has been studied on many surfaces as the decomposition product of ethylene. Although the formation of ethylidyne on Ru(001) from the dehydrogenation of ethylene has been studied using high resolution electron energy loss spectroscopy (HREELS) and reflection absorption infrared spectroscopy (RAIRS) in the past, there is a lack of agreement in the literature about the mechanism of ethylene decomposition.

In this study, reflection absorption infrared spectroscopy (RAIRS) and temperature-programmed desorption (TPD) were used to characterize and identify the surface intermediates formed in the thermal decomposition of ethylene (C2H4) on Ru(001). Ethylene is found to adsorb to the surface in a di-σ bonded complex at 95 K and dehydrogenates to form ethylidyne (CCHx) above 150 K. Upon further annealing the crystal to above 300 K, ethylidyne dehydrogenates to ethynyl (CCH). Annealing to higher than 450 K causes ethynyl to decompose to methylidyne (CH). The characterization of surface intermediates provides us with more insights into the thermal decomposition of ethylene on Ru(001), which is essential to reveal the reaction mechanism.

10:00am SS+AS+EN-MoM6 Kinetics of Alkyl Species on Pt(111), Yifeng Song, I.A. Harrison, University of Virginia

Kinetics of Alkyl Species on Pt(111)

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A heated effusive molecular beam was used to dose hot alkanes on to a relatively cold Pt(111) surface to overcome the initial activation barrier for dissociative chemisorption and to trap reactive intermediate species on the surface for subsequent spectroscopic and kinetic studies. Both reflection absorption infrared spectroscopy (RAIRS) and temperature programmed reaction (TPR) techniques were employed, in a complimentary way, to investigate the kinetics of alkyl fragments. Particular attention was paid to methylidyne (-C) decomposition kinetics, which have been proposed to be potentially rate-limiting in catalytic steam reforming of methane according to recent DFT calculations. Comparison between reforming kinetics of single crystal surfaces and nanocatalysts are presented. Elementary steps including the cleavage of C-H and C-C bonds in other C1, C2 and C3 reactive intermediates were also studied. The experimental findings, together with some theoretical work, provide molecularly resolved information relevant to catalytic reforming of light alkanes.

10:40am SS+AS+EN-MoM8 C2 Hydrogenation at Ambient Pressure on Pt(111), Joel Krooosyk, M. Trenary, University of Illinois at Chicago

Carbon has been shown to be the decomposition product from catalytic reactions involving hydrocarbons adsorbed on metal catalysts. Its presence reduces the amount of active surface sites available during a reaction. The decomposition products from adsorbed acetylene and ethylene on Pt(111) are C2 and C species, respectively. A previous UHV study showed that C2H2 adsorbed on Pt(111) at 750 K immediately decomposes to mostly C2 species. H2 was then coadsorbed with C2 at 85 K and annealed to 400 K, which reduced ethylidyne (C2H2), ethynyl (CCH) and methylidyne (CH) species. None of the species were hydrogenated to ethylene or ethanol, and after annealing to 750 K, a percentage of the carbon on the surface could be rehydrogenated after cooling the crystal to 300 K and coadsorbing H2.

In this study, the hydrogenation of C2 species in 1×10⁻³ to 1 Torr of H2 was monitored with RAIRS. The species was created on Pt(111) with CH2 adsorption at 750 K as done previously and the crystal was cooled to 300 K. The crystal was then annealed in an ambient pressure of H2. The C2 species are hydrogenated to ethylidyne at 400 K. C2H2 at approximately 450-500 K. This reaction is shown to be dependent on the pressure of H2. The results show that ethylidyne will be hydrogenated at 450 and 500 K at 1.0 and 1×10⁻² Torr H2, respectively. To show that the C2 species are fully hydrogenated and desorbed as ethane, which indicates that the surface is clean, CO was leaked into the cell with H2. We observe after the 500 K anneal that the peak assigned to the CO species is similar in intensity to one from CO adsorbed on a clean surface. This indicates that there are no C2 species remaining on the surface. Also, the peak positions of the terminal and bridge sites are shifted, which indicates that there is a high coverage of H atoms adsorbed on the surface.

11:00am SS+AS+EN-MoM9 Reaction Kinetics and Mechanism between Nitrate Radicals and Functionalized Organic Surfaces, Yafen Zhang, J.R. Morris, Virginia Tech

Interfacial reactions of nitrate radicals (NO3) with organic surfaces play an important role in atmospheric chemistry. To gain insight into the kinetic and mechanistic details, reactions between gas-phase nitrate radicals and model organic surfaces have been investigated. The experimental approach employs in situ reflection absorption infrared spectroscopy (RAIRS) to monitor bond rupture and formation while a well-characterized effusive flux of NO3 radicals impinges on the organic surface. Model surfaces are created by the spontaneous adsorption or thermal desorption of either vinyl-terminated alkanethiols (HS(CH2)nCH2CH3) or hydroxyl-terminated alkaniolthols (HS(CH2)nOH) onto a polycrystalline gold substrate. The H2C=CH-terminated self-assembled monolayers (SAMs) provide a well-defined surface with the double bond positioned precisely at the gas-surface interface. The surface reaction kinetics obtained from RAIRS revealed that the consumption rate of the vinyl radical was identical to the rate of oxidation of a surface-bound nitrate species and implies that the mechanism is one of direct addition to the vinyl group rather than hydrogen abstraction. Upon nitrate radical collisions with the surface, the initial reaction probability for consumption of carbon-carbon double bonds was determined to be (2.3 ± 0.5) X 10⁻². This rate is approximately two orders of magnitude greater than the rate of ozone reactions on the same surface, which suggests that oxidation of surface-bound vinyl groups by nighttime nitrate radicals may play an important role in atmospheric chemistry despite their relatively low concentration. In addition to studies involving the H2C=CH-terminated SAMs, we have probed the reaction dynamics of NO3 on HO-terminated SAMs. These experiments have revealed that the polarity of the terminal group has a large effect on the interfacial reaction rates. For the HO-terminated SAMs, the initial reaction probability was determined to be (5.5 ± 0.6) X 10⁻³ and the reaction mechanism appears to involve efficient hydrogen abstraction at the methylene group adjacent to hydroxyl terminus.

11:20am SS+AS+EN-MoM10 Oxide Growth Kinetics at SiO2/si(001) Interfaces Induced by Rapid Temperature Raising, Shuichi Ogawa, J. Tang, Tohoku University, Japan, A. Yoshigoe, JAEA, Japan, K. Nishimoto, Tohoku University, Japan, S. Ishizuka, Akita Nat. Coll. Technol., Japan, Y. Teraoka, JAEA, Japan, Y. Shuichi, Tohoku University, Japan

Thermal oxidation of Si is widely used in the fabrication of electric devices and MEMS. In the recent process, rapid thermal annealing (RTA) is used in a thermal oxidation process. In the RTA process, the temperature changes during the oxidation, but the temperature changing effects in the oxidation rate have not been cleared yet. In this study, the dependence of interface
oxidation kinetics on the temperature was investigated by real-time RHEED combined with AES to measure the oxide growth rate. Based on the activation energy and pre-exponential factor of the interface oxidation at SiO2/Si(001) interface, the rate-limiting reaction of the interface oxidation is discussed.

The oxidation experiments were performed with an apparatus equipped with facilities of RHEED combined with AES (Tohoku Univ.), and chemical bonding states including not only suboxide components but also strained Si atoms were investigated XPS at BL23SU, SPring-8. The clean Si(001) surfaces were oxidized by dry O2 gas at initial temperature T1. When the clean surfaces were completely oxidized, the temperature was raised from T1 to T2. T1 was changed between room temperature (RT) and 561 °C.

When temperature was raised from T1 to T2, the interface oxidation is enhanced. The initial oxidation rate after rising temperature k1 is discussed in this study. The k1 strongly correlates to the difference of T1 and T2. The Arrhenius equations between k1 and T2 are obtained in various T1. As the result, activation energy is obtained as 0.27 eV in good agreement with the previous experimental result[1] and theoretical study[2]. In addition, it is found that activation energy is independent from T1. On the other hand, pre-exponential factor decreases with increasing T1, decreasing by about one order when T1 increases from RT to 561 °C. In the XPS results, the Si4+ component increases and suboxide components and strained Si components (Si2 and Si3)[3] decrease with temperature elevation from 300 to 600 °C.

Based on these results, we propose the reaction between point defects (emitted Si atoms and its vacancies) generated by the oxidation-induced strain and O2 molecules as the rate-limiting reaction of the interface oxidation.

Dopants, Defects, and Interfaces in 2D Materials
Moderator: Jun Lou, Rice University

2:00pm 2D+AS+EM+NS+SS-MoA1 Cutting and Assembling 2 Nanometer Voids in Single Layer Hexagonal Boron Nitride, Thomas Greber, Y. Cun, M. Iannuzzi, A. Hemmi, J. Osterwalder, University of Zurich, Switzerland

Argon implantation beneath hexagonal boron nitride nanomesh on Rh(111) [1] leads to the formation of vacancy and interstitial defects [2]. The nanomesh is a single layer of hexagonal boron nitride on Rh(111), where 13x13 h-BN units accommodate on 12x12 Rh unit cells. The resulting super-honeycomb has a lattice constant of 3.2 nm and consists in regions where the h-BN “weaves” the Rh substrate (pores), and regions where h-BN is quasi freestanding (wires) [3].

The interstitial defects are called “nanotents”, where atoms are trapped beneath the ultimately thin “rainfly” made of a single layer of h-BN [2,4]. They are stable at room temperature and survive exposure to air.

The vacancy defects are sites where a boron or a nitrogen atom was kicked out by the Ar ion impact. If the implanted structures are annealed to 900 K the can-opener effect occurs: 2 nm h-BN flakes or “lids” are cut out of the h-BN nanomesh and 2 nm voids form [2]. At higher temperatures the resulting voids may diffuse and assemble, due to their repulsive interaction, in a super-superstructure with some order, i.e., a nearest neighbor distance of about 15 nm. Near the disintegration temperature of the h-BN nanomesh we finally observe self-healing of the voids in the nanomesh, which we assign to their annihilation in larger holes in the structure.

The report base on scanning tunneling microscopy, x-ray photoelectron spectroscopy, molecular dynamics and density functional theory calculations.

Financial support by the Swiss National Science Foundation and support by the EC under the Graphene Flagship (contract no. CNECT-ICT-604391) is gratefully acknowledged. We thank the Swiss National Supercomputer Centre (CSCS) for allocation of computer time.


Graphene’s atomic thinness makes it highly sensitive to surface adsorbates or defects within its carbon backbone. Aside from the known effects and impact on electronic properties, here we demonstrate the impact of defects on the mechanical properties and the response of mechanical resonators. In particular, once defects are formed in atomically-thin materials they can be quite mobile and form more complicated defect structures such as bi- or tetra-vacancy clusters. We execute experiments using mechanical drum resonators made from single- to multi- to many-layer graphene systems. We use both CVD grown graphene and reduced graphene oxide (rGO) films to capture a wide range of defect structures. By measuring the fundamental frequency response of the resonators (in the MHz range) we extract properties such as tension, quality factor, and modulus as a function of external manipulation [1]. For highly defective rGO films measuring 10-40nm thick, we can tune the frequency response by 500% and quality factor by 20x through laser annealing, which effectively rearranges defects throughout the film [1]. Alternatively, using graphene 1-4 layers thick, we find the resonator response is significantly more sensitive to the formation and annihilation of meta-stable defects, such as the tetra-vacancy structure. We will show how the defect mobility and resonator response changes with different energy photons and come to understand these differences based on calculated defect migration energies of different defects types in graphene.


3:00pm 2D+AS+EM+NS+SS-MoA4 Graphene Cleaning using a Low Energy Ar Ion Beam, KiSook Kim, G. Yeom, Sungkyunkwan University, Republic of Korea

Recently, graphene has been widely investigated due to the superior electrical, mechanical, thermal, and chemical properties. Especially, CVD graphene which was grown on Cu foil and transferred to various substrates using PMMA has been used most widely due to the possible large area applications such as electronic devices for displays, semiconductors, etc. However, in order to apply the transferred CVD graphene to the various electronic device fabrication, PMMA residue on the graphene surface formed during the transfer process and lithography process needs to be completely removed without damage. Various methods have been investigated to remove the residue on the graphene surface such as current cleaning, heat treatment, chemical cleaning, etc. However, it is reported that these methods are not effective in removing the residue on graphene or not applicable to industry.

In this study, a controlled Ar ion beam has been used to effectively remove the PMMA residue on graphene surface. By controlling the Ar ion beam condition, the residue on graphene surface could be removed while minimizing the damage on the graphene surface. Especially, by lowering the Ar beam energy less than 10 eV, it was possible to effectively remove the PMMA residue without damaging the graphene. The removal of PMMA residue on the graphene surface could be identified using Raman Spectroscopy showing the red shift of 2D peak (2670 cm⁻¹) and blue shift of G peak (1600 cm⁻¹) in addition to the decrease of RMS roughness from 1.3nm to 0.3nm using an AFM (Atomic Force Microscopy). The effectiveness of graphene cleaning was also confirmed by XPS (X-ray Photoelectron Spectroscopy), by the uniform deposition of ALD HfO₂ layer on the cleaned graphene surface, by measuring the electrical properties of deposited ALD HfO₂, etc.

3:40pm 2D+AS+EM+NS+SS-MoA6 Electronic Structure Modification in van der Waals Heterostructures: Interlayer Hybridization and the Case of Graphene/MoS₂, Matthias Battill', H. Cey-Diaz, University of South Florida, M.C. Asensio, Synchrotron Soleil, France, J. Avila, Synchrotron Soleil

Artificial van der Waals heterostructures promise to combine materials with diverse properties. Simple mechanical stacking or conventional growth of molecular hetero-layers would enable fabrication of novel materials or device-structures with atomically precise interfaces. Because covalent bonding in these layered materials is limited to molecular-planes, interface interactions between dissimilar materials are expected to modify the properties of the individual layers only weakly. Here we prepare graphene/MoS₂ heterostructures by transferring CVD-grown graphene onto a MoS₂ substrate. It is shown that high quality interfaces between graphene and MoS₂ can be obtained by UHV annealing. The quality of the graphene is confirmed by atomically resolved tunneling spectroscopy and the MoS₂ substrate by angle resolved photoemission spectroscopy (ARPES) and nano-ARPES utilizing a focused photon beam at the SOLEIL synchrotron. We show that at the Fermi-level graphene exhibits a perfect, gapless and undoped Dirac-cone. However, in regions where the x-band of graphene overlaps with states of the MoS₂ substrate, opening of several band-gaps are observed. This demonstrates that the electronic properties in van der Waals heterostructures can be significantly modified by interlayer interaction and thus exemplifying opportunities for tuning materials properties of graphene and other 2D-materials by interfacing them with dissimilar van-der Waals materials.

4:00pm 2D+AS+EM+NS+SS-MoA7 Edge States and Exposure to Hydrogen of Silicon at the 2D Limit on Ag(111), A.J. Mannix, B.T. Kiraly, Argonne National Laboratory, M.C. Hersam, Northwestern University, Nathan Guisinger, Argonne National Laboratory

Chemical functionalization of atomically thin materials results in significant modifications to their electronic properties, which can be exploited in device applications. Compared to the chemical inertness of graphene, 2D silicon is expected to exhibit greater reactivity, and thus a greater amenability to chemical functionalization. Among potential functionalization chemistries, hydrogen termination is favored for its relative simplicity and proven efficacy with graphene and bulk Si surfaces. Using ultra-high vacuum (UHV) scanning tunneling microscopy (STM), we have studied the temperature-dependent effects of exposing 2D silicon platelets grown on Ag(111) to molecular and atomic hydrogen. At low doses, atomic hydrogen results in limited adsorption and temperature dependent etching. In the bulk, the formation of vacancies and extended...
etch pits is observed. In addition, edge states can play a critical role in the electronic properties of 2D materials. We have also examined at the atomic-scale the edges of 2D silicon platelets.

4:20pm 2D+AS+EM+NS+SS-MoA8 Chlorine Trap-Doping for Transparent, Conductive, Thermally Stable and Damage-Free Graphene, Pham Viet Phuong, K.N. Kim, M.H. Jeon, K.S. Kim, G. Yeom, Sungkyunkwan University, Republic of Korea

We propose a novel doping method of graphene by cyclic trap-doping with low energy chlorine adsorption. Low energy chlorine adsorption for graphene chlorination avoided defect (D-band) formation during doping by maintaining the π-bonding of the graphene, which affects conductivity. In addition, by trapping chlorine dopants between the graphene layers, the proposed doping method dramatically decreased the sheet resistance by ~88% at an optimized condition. Among the reported doping methods including chemical, plasma, photochemical methods etc., the proposed doping method is believed to be the most promising for producing graphene of extremely high transmittance, low sheet resistance, high thermal stability, and high flexibility for use in various flexible electronic devices. Results of angle resolved X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron spectroscopy (HR-TEM), Raman spectroscopy, ultraviolet-Visible spectroscopy (UV-Vis) and sheet resistance, showed that this method is also non-destructive and controllable. The sheet resistance of the doped tri-layer graphene was 70 Ω/sq at 94% transmittance, which was maintained for more than 6.5 h at 230°C. Moreover, the defect intensity of graphene was not increased during the cyclic trap-doping.

4:40pm 2D+AS+EM+NS+SS-MoA9 Modification of Graphene by Neutral Beam Irradiation and Edge Structure Analysis, Takeru Okada, S. Sumakawa, Tohoku University, Japan

Since the discovery of single layer of Graphite, graphene, a single layer of hexagonal carbon atoms, has attracted much attention and shown exciting specific properties. Graphene is a zero band gap semiconductor. Therefore band gap control is one of most important issue to apply for electronic device applications. In order to construct electronic devices with logic operation, both p- and n-type conductions and the control of the carrier density in an active channel are required. Doping with foreign atoms, such as N and B, has proven to be an effective way to modify the electronic properties of carbon related materials and extend their applications. In particular, nitrogen doping brings a carrier which could turn carbon nanotube into n-type semiconductors. It is also feasible to modify the electronic properties of Graphene. Although several doping methods have reported so far, process damages (defect generation) cause degradation of electronic properties.

In this paper, we introduce ultra-low damage neutral beam system which consists of a plasma and process chambers that are separated by a carbon aperture charged with ions. Nanostructures and ultra-violet photoemission from the plasma can be effectively eliminated by the aperture. As a result, only the neutral beam arrives the surface of the sample at the substrate in the process chamber. We used nitrogen gas for plasma generation and adopted multi-layer Graphene to investigate nitridation mechanism. Graphene multi-layer was irradiated by nitrogen neutral beam with controlled energy of 10 eV at room temperature. The surface modification was analyzed by x-ray photoelectron spectroscopy (XPS). XPS analysis indicated that the carbon atoms were substituted to nitrogen atom and atomic concentration of nitrogen reaches 15 %. Additionally, bonding state of C and N was found to depend on neutral beam irradiation time. Thus beam energy controlled neutral beam can selective nitridation of Graphene. Furthermore the doping density is estimated by Raman spectroscopy and result in 10^13 [cm²], which is enough to n-type doping of Graphene.

5:00pm 2D+AS+EM+NS+SS-MoA10 Growth Mechanism of Metal Clusters on a Graphene/Ru(0001) Template, Shixuan Du, L.Z. Zhang, Chinese Academy of Sciences, W. Hofer, University of Liverpool, UK, H.J. Gao, Chinese Academy of Sciences

Metal nano-clusters have attracted considerable interest because of the potential applications in catalysis and information storage. Due to the soft nature of epitaxial graphene and the lattice mismatch between graphene and metal substrates potential moiré patterns can be formed. A graphene/metal template, moiré template, can be used to grow dispersed metal nano-clusters with controllable size and shape, or metal clusters with large size and metal layers. However, how intrinsic properties of metal atoms and the moiré template influence the selective adsorption and the growth mode of metal clusters is still open to debate. A general rule, predicting the morphology of metal nano-clusters on a G/metal surface, important to guide experimenters, is still missing. Using first-principles calculations combined with scanning tunneling microscopy experiments, we investigated the adsorption configurations, electronic structures and the corresponding growth mechanism of several transition metal (TM) atoms (Pt, Ru, Ir, Ti, Pd, Au, Ag, and Cu) on a graphene/Ru(0001) moiré template (G/Ru(0001)) at low coverage. We find that Pt, Ru, Ir, and Ti selectively adsorb on the fcc region of G/Ru(0001) and form ordered dispersed metal nano-clusters. This behavior is due to the unoccupied d orbital of the TM atoms and the strong sp^2 hybridization of carbon atoms in the fcc region of G/Ru(0001). Pd, Au, Ag, and Cu form nonselective structures because of the fully occupied d orbital. This mechanism can be extended to metals on a graphene/Rh(111) template. By using Pt as an example, we provide a layer by layer growth path for Pt nano-clusters in the fcc region of the G/Ru(0001). The simulations agree well with the experimental observations. Moreover, they also provide guidance for the selection of suitable metal atoms to form ordered dispersed metal nano-clusters on similar templates.

References:
1. L.Z. Zhang et al. Advanced Materials Interfaces, accepted.

Actinides and Rare Earths Focus Topic

Monday Afternoon, November 10, 2014

2:00pm AC+AS+MI+SA+SS-MoA Theoretical Modeling of f Electron Systems
Moderator: Ladislav Havela, Charles University, Czech Republic

The correlated band theory implemented as a combination of the local density approximation with the dynamical mean-field theory is applied to PuO2. We obtain an insulating electronic structure consistent with the experimental photoemission spectra, and a nonmagnetic ground state that is characterized by a noninteger filling of the plutonium f shell (n_f ≈ 4.4). Due to a sizable hybridization of the f shell with the p states of oxygen, the ground state is more complex than the four-electron Russell–Saunders 1^+_s manifold split by the crystal field. The dynamical mean-field theory, which in the present case can be schematically viewed as an extension of the crystal-field model with hybridization terms, improves the agreement between the theory and experiment for the magnetic susceptibility [1]. Encouraged by the good accuracy achieved for PuO2, we apply the theory to several other tetravalent actinide oxides.


2:40pm AC+AS+MI+SA+SS-MoA3 DMFT Modeling of Electronic Spectral Properties in Pu-based Actinides, Jian-Xin Zhu, Los Alamos National Laboratory

In this talk, I will present a study of the electronic structure of Pu metals and its 115 compounds in the framework of the combination of local density functional approximation and dynamical mean-field theory. In particular, the results on momentum-resolved spectral functions will be presented and be compared with those based on the LDA only. In addition, the effect of Pu 5f electron occupancy on the electronic structure of these systems will also be discussed. The test of these results by future angle-resolved photoemission spectroscopy measurements will give a stringent constraint on the theoretical approach.

3:00pm AC+AS+MI+SA+SS-MoA6 The Evolution in Pu Nanocluster Electronic Structure: From Atomicty to Three-Dimensionality, James Tobin, S.W. Yu, B.W. Chung, Lawrence Livermore National Laboratory, M.V. Ryzhkov, Russian Academy of Science-Urals, A. Mirmelstein, Russian Federation Nuclear Lab (VNIITF)

The development of electronic structure in solid systems as a function of size has long been a subject of great interest and extensive scientific investigation. Experimentally, the transition from nanoscale or mesoscopic to bulk behavior in metal clusters, was reported in 1981 by Mason and co-workers. Similarly, the evolution from two-dimensional to three-dimensional band structure in metal overlayers and the manifestation of nanoscale effects in compound semiconductor have also observed. In the
area of actinide materials, the progress has been slowed by the limitations imposed by the highly radioactive, chemically toxic and pyrolytic nature of these materials. However, recent theoretical studies include UO2 molecules, solid actinide oxides, and actinide carbide clusters. A new approach to cluster calculations has been taken in this study. Past cluster calculations were arranged in such a way that the central atom would exist in a bulk like environment. In calculations herein, it is expected that the central atom will be in the most bulk-like environment as well. However, just as in any finite size object, there will be variation of potential at the positions of symmetry non-equivalent atoms within the simulated cluster. Hence, averaging over all of the atoms in the cluster will give a measure of the effect of size. We will use this aspect of cluster calculations to investigate size related effects. Here, we report the result of the calculation of the electronic structure of clusters of Pu and their comparison to bulk spectroscopic results. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract No. DE-AC52-07NA27344. Work at the RAS and VNIITF was supported in part by Contract B590089 between LLNL and VNIITF. The Advanced Light Source (ALS) in Berkeley and the Stanford Synchrotron Radiation Laboratory are supported by the DOE Office of Science, Office of Basic Energy Science. For more detail see: M.V. Ryzhkov, A. Mirmelstein, S.-W. Yu, B.W. Chung and J.G. Tobin, “Probing Actinide Electronic Structure through Pu Cluster Calculations,” Inl. J. Quantum Chem. 113, 1957 (2013); COVER ARTICLES.

4:20pm AC+AS+MI+SA+SS-MoA8 Electronic Structure, Magnetic Properties, and Magneto-Structural Transformations of Rare Earth Magnetocalaric Materials Durga Pandey, Ames Laboratory, I.A. Pecharsky, K.A. Gschneidner, Jr., Ames Laboratory and Iowa State University INVITED

We present first principles modeling of structural and magnetic properties of Gd3Ga5 based magneto-calaric materials. The total energy as a function of the shear displacement of slabs confirms stability of experimentally observed magnetic and magnetic structures. Small substitutions of the Gd by Y and Lu lead to a catastrophic loss of ferromagnetism, but the substitutions by La have no effect on the magnetism. Furthermore, substitutions of the Ge by Si exert chemical pressure and transform the antiferromagnetic O(H) to the ferromagnetic O(I) ground state. In addition, we present a pathway for estimating the magnetic entropy change in the room temperature giant magnetocaloric compounds, i.e. Gd3Si2Ge2, by coupling first principles outputs with the established magneto-thermodynamic models. The theoretical values of the magnetic entropy change compare well with experimental results.

This work was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. The research was performed at the Ames Laboratory, which is operated for the U.S. DOE by Iowa State University under contract # DE-AC02-07CH11358.

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

The Liquid Interface & Depth Profiling and Sputtering with Cluster Ion Beams

Moderator: Ian Gilmore, National Physical Laboratory, Michaelaen Pachsloki, The Dow Chemical Company

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

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

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

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

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

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

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

INVITED

Argon cluster sources suitable for depth profiling organic materials have developed rapidly and are now widely available and routinely used to analyse materials ranging from organic electronic devices to biological samples. This fantastic progress allows detailed insight into the chemistry and structure of organic materials with depth resolutions below 10 nm over many micrometres. When combined with 2D surface chemical imaging, detailed 3D reconstructions can be obtained allowing the label-free visualization of chemical distributions for applications in many areas. In this presentation, we show that with gentler ions, where the energy per atom can be as low as 5-40 eV, it is possible to greatly reduce bulk damage and the preferential removal of weakly bound elements in complex materials.1

References:

4:20pm AS+BI+MC+SS-MoA8 Argon Clusters - A Novel Solution for Mass Spectrometric Characterization of Crosslinking Organic Multilayers: Comparison with C{sub 60} and Argon Cluster Sputter Sources, Shin Miyamoto, National Institute of Standards and Technology (NIST), D. Rading, ION-TOF GmbH, Germany, B. Bush, G. Gillen, National Institute of Standards and Technology (NIST), D.G. Castner, University, Germany

A model organic layer system consisting of three 1 nm delta layers of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) separated by three 30 nm layers of tris(8-hydroxyquinolinato)aluminum (Alq3) was used to evaluate the effectiveness of helium low temperature plasma (LTP) etching for the preparation of crater edge surfaces for subsequent compositional depth profile analysis. The quality of the depth profile was determined by comparing the depth resolutions of the BCP delta layers obtained from the plasma-etched craters with those obtained using ToF-SIMS dual-beam depth profiling equipped with C{sub 60} and argon cluster (AETOF s′ 200) sputter sources. Using the full width at half maximum (FWHM) of each delta peak, the depth resolutions of the second and third delta layers were measured to be 6.9 nm and 6.0 nm for the plasma-etched crater, respectively, which were very close to the depth resolutions of 6.2 nm and 5.8 nm obtained from the argon cluster sputter source. In contrast, the use of a 1/e decay length to approximate the depth resolution gave results that identified the artifacts caused by ion bombardment in SIMS depth profiling. The 1/e decay length for the trailing edge of each delta were 2.0 nm and 1.8 nm for the plasma-etched crater, respectively, while the argon cluster depth profile gave decay lengths of 3.5 nm and 3.4 nm, owing to the longer tails produced by argon clusters and Argon sputter damage. For the C{sub 60} depth profile, the need to resolve the as a result of a 20% nonlinear sputter rate gave artificially improved depth resolutions, where FWHM of the delta peaks were 5.6 nm and 7.3 nm, respectively, and 1/e decay lengths were 1.7 nm and 2.3 nm, respectively. Although some artifacts such as contaminant deposition remain, low temperature plasma was shown to be a viable option for creating crater edges for compositional depth profiling without artifacts seen in ToF-SIMS depth profiling.

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

Desorption and ionization induced by neutral clusters (DINeC) can be employed as a soft and matrix-free method for transferring surface-adsorbed biomolecules into the gas phase. Using neutral clusters with polar constituents such as SO_{3}, the impacting clusters do not only provide the energy necessary for desorption but also serve as a transient matrix in which the desorbing molecule is dissolved during the desorption process. As a consequence, desorption and ionization of oligopeptides and smaller proteins can proceed at comparably low energies of the impacting clusters and without any fragmentation [1]. Using a combination of DINEC and ion
Biomaterial Interfaces

**Room: 317 - Session BI+AS+NS-MoA**

**Bio/Nano Interfaces**

**Moderator:** Patrick Koelsch, University of Washington

2:00pm **BI+AS+NS-MoA1** Controlling Bio/Nano Interface Response using Metal Oxide Atomic Layer Deposition: Zinc Oxide ALD Modifies how Human Lung Fibroblasts respond *In Vitro* to Multiwall Carbon Nanotubes, Erin Dandley, A. Taylor, G.N. Parsons, J. Bonner, North Carolina State University

Carbon nanotubes have been reported to cause pulmonary fibrosis in mice after inhalation exposure. When inhaled, multiwall carbon nanotubes (MWCNTs) activate macrophage inflammasomes and interleukin (IL)-1β release, key cellular components of the innate immune response. Macrophages are the first line of defense that engulf and remove inhaled MWCNTs from the lungs. Macrophages are also a source of secreted osteopontin (OPN), which promotes tissue matrix remodeling and fibrosis. These responses may be triggered by the unique aspect ratio, aggregation or surface chemistry of MWCNTs. In previous studies, we explored atomic layer deposition (ALD) as a means to modify the surface functionality of MWCNTs and studied how the surface coating affected the toxic response of THP-1 cells, a widely used human monocyte/macrophage cell line, and primary peripheral blood monocytes (PBMCs) obtained from normal human donors. Compared to uncoated MWCNTs, we found that nanotubes with AIOx nanocoatings showed enhanced IL-1β release and decreased OPN production in THP-1 cells and PBMCs, indicating that the coating enhances the innate immune response and decreases pro-fibrotic activity.

In this study we examined the effect of ALD ZnO coatings on the fibrogenic response in human lung fibroblast (HLFs) using mRNA expression and secretion of transforming growth factor (TGF)-β1 and CXCL11, mediators that promote and deter fibrosis respectively. We find that the ALD ZnO layer thickness can be controlled down to ~5nm, and the thickness scaled directly with number of ALD cycles, as observed by TEM. Thicker coatings inhibited MWCNT aggregation, and sonication allowed us to induce fragment generation. In this way the ALD coating allowed us to independently adjust surface termination, fiber aggregation, and fiber aspect ratio, providing us a unique tool to examine how each of these factors influences cellular response. Initial results show that the ZnO coating significantly increased TGF-β1 mRNA expression and stimulated a larger pro-fibrogenic response in HLFs compared to uncoated MWCNTs. Control experiments using ZnO nanoparticles also showed potent induction of TGF-β1 mRNA in HLFs. Also, the response tends to correlate with extent of dispersion, and is nearly independent of MWCNT aspect ratio. These experiments show that nanoscale surface functionalization of nanoscale materials may help us gain better understanding of the mechanisms associated with toxicity of nanomaterials, and expand knowledge of biological response at nano/bio interfaces.

2:20pm **BI+AS+NS-MoA2** Mechanically Optimized Fe (III) Doped Silica Nanoshells as a Contrast Agent for Ultrasound Imaging and HIFU Therapy, James Wang, A. Liberman, R. Viveros, C. Barback, S.L. Blair, Z. Wu, R. Mattrey, W. Trogler, A.C. Kummel, University of California at San Diego

Ultrasound (US) is a common medical imaging modality due to its flexibility, low-cost and therapeutic potential. 500 nm silica nanoshells were synthesized as a contrast agent to improve US imaging signal for better diagnostic performance. Iron (III) was included into the silica network to enhance the biodegradability of the silica nanoshells. Previously, ferric iron was shown to facilitate silica nanoshell biodegradation due to its strong binding affinity with serum transferrin proteins. The removal of iron from the silica network by serum proteins fragments the nanoshells enabling effective biodegradation for *in vivo* applications. The silica nanoshells are filled with perfluorocarbon (PFC) vapor which expands and shatters the nanoshells during US irradiation. A mechanically weaker silica nanoshell increases US signal at lower power. A range of alkoxysilanes with selected R-groups such as long chain hydrocarbons, fluorinated carbon chains, fluorinated phenyl groups and vinyl groups were employed along with tetramethyl orthosilicate and iron (III) ethoxide in a modified sol-gel synthesis to create structural defects that alter the mechanical properties of the nanoshells. Monodisperse 500 nm polystyrene beads were used as a soft template during the reaction. The silica nanoparticles were calcined at 550°C to remove the polystyrene core and form hollow nanoshells. SEM and TEM showed that 500 nm silica nanoshells with different microstructures were synthesized incorporating alkoxysilanes with different R-groups. Formulations with higher concentrations of alkoxysilanes with large R-groups such as long chain hydrocarbons resulted in stronger *in vitro* contrast enhanced ultrasound (CEUS) signals due to the increase of...
structural voids that resulted in weaker shell strength. CEUS experiments demonstrated that mechanically weaker silica nanoshells exhibited longer signal life time and required a lower mechanical index (MI) for imaging. The high intensity focused ultrasound (HIFU) properties of the modified silica nanoshells were tested for potential therapeutic applications. Mechanically weaker silica nanoshells were shown in vitro to require a lower HIFU power to fracture which is consistent with safer HIFU therapy. By synthesizing strength tunable silica nanoshells as US contrast agents, it is possible to improve diagnostic performance in clinical applications, such as smaller tissue structures or early stage tumors. Additionally, mechanically weaker silica nanoshells may also increase the efficiency of HIFU enabling HIFU at lower US power and/or higher speed.

2:40pm Bi+AS+NS-MoA3 Synthesis, Functionalization, and Biological Imaging with Quantum Dots, Preston Snee, University of Illinois at Chicago

INVITED

Semiconductor quantum dots (QDs), or nanocrystals, are versatile color tunable fluorophores that possess unlimited potentials in alternative energy generation and for biological sensing and imaging applications. Our group has made advances in the synthesis QDs to produce 100% efficient emitters; furthermore, we can dope the semiconductor with guest ions to alter the bandgap. We recently invented a method to dope each quantum dot with an exact number of guest ions, a feat that was previously considered impossible. As very bright fluorophores, quantum dots are ideal for biological imaging and sensing. Our first contribution in this regard was to develop methods of chemical and biological functionalization of water-soluble quantum dots as many existing methods either quenched the QDs or had very low reaction yields. We have circumvented these problems by synthesizing polymers which serve as QD functionalization reagents; the poly(d-lysine) used in DLS imaging has an intermediate stability and allows us to conjugate chemical and biological vectors to the nanocrystals with >100% reaction yields. We use these methods to functionalize QDs with organic fluorophores that can report on the local chemical and biological environment. We have synthesized several ratiometric, or “self-calibrating” sensors, for pH, toxic metals, DNA, and proteins. In our recent work on protein sensing, we have developed an all optical method for sensing unlabelled proteins by detecting the relatively better detecting profile of our currently existing technology. We have also circumvented the well-known problem of cytocellular delivery of quantum dots into live, adherent cells.

3:40pm Bi+AS+NS-MoA6 Easynanofab: Fast, Simple, Combinatorial Routes to Reusable Plasmonically Active Gold Nanostructures Over Macroscopic Areas, A. Tsargorodska, O. El Zubir, Graham Leggett, University of Sheffield, UK

Plasmonic effects associated with gold nanocrystals have attracted widespread interest for the interrogation of biological molecules. Existing approaches to fabrication of plasmonic nanostructures fall into two categories: high precision methods such as electron beam lithography that rely on complex, specialised infrastructure; and simple, low-cost methods such as colloidal lithography that offer limited capacity. Here, we describe a fast, simple method for the fabrication of re-usable, robust, macroscopic nanostructures over macroscopic (cm$^2$) areas that provides enormous scope to control nanostructure morphology and dimensions, and which also uses only simple apparatus and requires no access to a clean-room. We have assembled a combinatorial library of over 200 different samples consisting of highly crystalline gold nanostructures that exhibit varying morphologies, dimensions and periodicities but yield intense plasmon bands. These structures enable the rapid identification of optimum substrates for the detection and analysis of biological targets, and provide a platform for exploring the relationship between particle morphology and optical properties. Self-assembled monolayers (SAMs) of alkylthiolates on chromium-primed polycrystalline gold films are patterned using a Lloyd’s mirror interferometer and etched using mercaptohexylamine in ethanol in a fast, simple method. The use of a Cr adhesion layer facilitates the cleaning of specimens by immersion in piranha solution, enabling their repeated re-use without significant change in their absorbance spectra over two years. Annealing yields structures with a uniformly high degree of crystallinity that exhibit strong plasmon bands. Because of the ease with which nanoparticle morphology may be controlled using interferometric lithography (IL), this provides a convenient means to investigate the correlation between structural parameters (particle dimensions, spacing) and optical responses. The shift in the position of the plasmon band after site-specific attachment of histidine-tagged green fluorescent protein (His-GFP) and after adsorption of chlorophyll and bacteriochlorophyll was measured for a range of nanostructured films, enabling the rapid identification of structures that yield the largest shifts. X-ray absorption resonances were observed when light-harvesting membrane protein complexes from plants and bacteria were coupled to gold nanostructure arrays, yielding absorbance spectra that were very different from those of the clean gold nanostructures. This approach offers a simple route to the production of durable, reusable, macroscopic arrays of gold nanostructures with precisely controllable morphologies.

4:00pm Bi+AS+NS-MoA7 Impacts of Nanoparticle Synthesis Route, Structure and Serum Proteins on the Dispersion and Dissolution of Ag Nanostructures, M. Wang, Pacific Northwest National Laboratory, A. Porter, M.P. Ryan, Imperial College London, UK, M.H. Engelhard, Pacific Northwest National Laboratory, A.E. Porter, M.P. Ryan, Imperial College London, UK, Donald Baer, Pacific Northwest National Laboratory

The widespread use of silica nanoshells in consumer products raises questions of environmental impact and toxicity. Because both silver nanoparticles, and silver ions formed by particle dissolution, may impact biological systems, it is important to understand the characteristics of silver nanoparticles as they are made and their stability and dissolution in the medium relevant to environmental and toxicological studies. Silver nanoparticle synthesis routes have a strong impact on the size, shape and varying physical and chemical characteristics. In this talk we will summarize the characterization and dissolution stability of three types of silver nanoparticles (20 nm particles synthesized with and without gold core (~7 nm) and 110 nm particles with gold core) in cell culture media with serum proteins: FBS10%/RPMI, the culture media used at Pacific Northwest National Laboratory for in-vitro toxicity studies. These nanoparticles were synthesized and prepared for biological study in aqueous solution. They were examined in situ using dynamic light scattering, zeta potential measurements and optical adsorption and ex situ with x-ray photoelectron spectroscopy and transmission electron microscopy. For the dissolution studies, concentrations of particles examined were varied from 1 μg/ml to 50 μg/ml, consistent with the range of concentrations typically used by drug and nanoparticles with a smaller crystallite size and higher apparent solubility than three different batches of pure ~ 20 nm silver particles. A simple dissolution model was found to describe the particle size variation of silver and amount of dissolved silver for particle loadings above 9 μg/ml. The effective solubility product obtained from fitting the data was higher for the 20 nm particles with the gold core in comparison to the pure silver, 110 nm particles. The dissolution of silver was also found to be dependent on the presence of serum proteins contained in fetal bovine serum (FBS). In addition, the protocol of dispersion in cell culture medium was found to influence particle agglomeration and the rate of dissolution. In these measurements focusing on a 24 hour time point, we found that the structure of the formed nanoparticle can have a significant impact on the concentration of dissolved silver in media and thus the dosimetry to which cells would be exposed during in vitro studies. This work has been supported by the NEHS under Center grant U19 ES019544. Portions of this work were performed using EMSL, a national scientific user facility sponsored by the US Department of Energy, Biological and Environmental Research and located at PNNL.

4:20pm Bi+AS+NS-MoA8 Analysis of Protein Coated Nanoparticles by X-ray Photoelectron Spectroscopy and Solution-Based Particle Size Techniques, C. Minelli, Natalie Betsey, A.G. Shard, National Physical Laboratory, UK

The attachment of proteins to nanoparticles’ surface is of increasing interest in medicine for applications such as drug delivery and diagnostics. The unintentional acquisition of a protein corona from biological media is also important in determining the performance and potential toxicity of such particles. Understanding and refinement of the performance of nanoparticles of use in medical applications require accurate and quantitative characterisation of their protein interface. Our efforts are focussed upon developing measurement techniques to enable useful characterisation of this interface. In this study, three biomolecules of a range of sizes, shapes and mechanism of interaction with gold surfaces, i.e. 16 AA peptide, BSA and IgG, were adsorbed to gold nanoparticles (10, 20, 40, 60 and 80 nm) and the shell thickness was measured in solution using dynamic light scattering (DLS) and differential centrifuge sedimentation (DCS). UV-visible spectrophotometry was used to monitor localised surface plasmon resonance (LSPR) shifts of the nanoparticles due to the acquisition of the protein shell. Combination of this information with thickness measurements allowed for an estimation of the protein shell refractive index and average number of biomolecules at the nanoparticle surface. X-ray photoelectron spectroscopy (XPS) analysis of the same nanoparticles deposited on a PtFE substrate enabled determination of the nanoparticle shell chemical composition and dehydrated thickness, from which the number of molecules at the nanoparticle surface was also estimated. Parallel characterisation of the nanoparticles in their colloidal form and in vacuum provided consistent results and the combination of the techniques revealed further insight into molecular adsorption at nanoparticles’ interfaces. The complementarity of the approaches also allowed for validation of the methods, which is important for their application to a wide range of
nanoparticle types. For example, DLS and LSPR analysis are not suitable in a cellular context. By using precision hydrodynamic flows, we demonstrated that we can distinguish dense and sparse binding modes and formation must overcome the challenge of very low effective mobility of DNA. Organization is driven by the specific binding of proteins to form tertiary structural properties of the electrospun meshes influence bacterial attachment, proliferation and growth.

5:00pm BI+AS+NS-MoA10 Electrophoretic Stretching of Tethered DNA in Nanoslits, Jia-Wei Yeh, K. Szeto, H.G. Craighead, Cornell University

We have investigated the field-extension of tethered DNA in nanoslits with slit heights ranging from 30 to 130 nm, and performed an analysis from an approximated modified worm-like chain (mWLC) field-extension relation. DNA molecules confined to microspheres were anchored at a micro-nanoconfined interface and the molecules electrohydrodynamically extended. We demonstrated that both the DNA segmental correlation and equilibrium lengths increased as the slit height decreased. Furthermore, we observed confined DNA where \( h \geq 30 \) nm, we observed reptation of the DNA's contours within the nanoslit, a phenomena that may be induced by inhomogeneous surface charge distributions. This nano-confined system may have implications for single-molecule sensors on detecting and analyzing genetic, epigenetic markers, and related nanobiotechnological applications.


DNA performs a carefully choreographed ballet during the cell cycle. The organization is driven by the specific binding of proteins to form tertiary DNA-protein-DNA complexes. The search process that precedes the formation must overcome the challenge of very low effective mobility of genomic-sized DNA pieces in the dense cellular environment. In this paper we will discuss a group of nanofluidic device that force two DNA molecules to either slide past each other in parallel, or cross over each other at a steep angle. Nanochannel cross-sections are 100x100 nm², and are hundreds of microns long. Because DNA is elongated through confinement, loop with a length down to 2 kb can be directly observed in real time. Channels are made of fused silica, enabling single-molecule observation of both DNA and proteins. Because the effective concentration of DNA inside channels exceeds 1 mg/ml with the channel at the point of DNA-DNA contact, protein-mediated capture cross-sections are very high.

We will present analyses of different DNA-binding proteins that we can distinguish dense and sparse binding modes and the compensation of electrostatic DNA-DNA repulsion through protein binding. We further report the detection of long-lived tertiary complexes acting as a lock for looped DNA configurations, and the presence of very short-lived transient links. We further demonstrate a pathway for loop formation that is enhanced in nanochannel devices, and that may be important in a cellular context. By using precision hydrodynamic flows, we are able to measure free energies of the search process.

Materials Characterization in the Semiconductor Industry Focus Topic

Room: 313 - Session MC+2D+AP+AS-MoA

Characterization of III-Vs (2:00-3:20 pm)/Photovoltaics, EUV masks, etc. (3:40-4:40 pm)

Moderator: Alain Diebold, SUNY College of Nanoscale Science and Engineering, Paul van der Heide, GLOBALFOUNDRIES, NY, USA

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

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

Ion beam sputtering of III-V compounds is intrinsically more complex than in conventional Si substrates. One of the major issues with depth profiling of III-V materials is their higher sensitivity to formation of ion-beam induced topography, which has a detrimental impact on depth resolution [2]. We have previously reported anomalous sputtering behavior of (In)GaAs under low energy O⁺ sputtering, causing severe degradation of depth resolution [3]. In case of low energy Cs⁺ sputtering at oblique incidence, we have achieved uniform sputtering conditions on different III-V compounds with no significant topography formation. We have demonstrated constant depth resolution in III-V multilayer structures with decay lengths as low as 2 nm/decade at low Cs⁺ impact energy (down to 250 eV).

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

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

assessed the substitutional incorporation of the nitrogen throughout the thickness of the 100–400 nm thick films.


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

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

In one experiment we determined the transition between Ga- and N-rich MBE growth conditions of GaN by setting a fixed N-flow that generated a steady-state background chamber pressure of 1.5x10⁻⁶ Torr, while the Ga-source was set up to generate a linear flux ramp from 9.8x10⁻⁶ to 3.9x10⁻⁴ am/s over two hours. During this ramp, the Auger electron signals for N (375 eV) and Ga (1050 eV) were continuously monitored. As expected, both the Ga and N signals increased as a GaN film was starting to form under N-rich conditions and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N-rich and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N-rich and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N-rich and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N-rich and subsequently stabilized. At about 80 min the N-signal started decreasing, which we define as the boundary between N-rich and subsequently stabilized.

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


III-N materials continue to play a significant role in a range of technologies from rf electronics to visible and UV emitters and detectors. This is true despite a heavy population of extended defects in the active regions of these devices, which degrade the operation, potential performance, and reliability of such devices. With such high dislocation densities when grown heteroepitaxially on sapphire or SiC (10⁸-10¹⁰ cm⁻²), techniques to reliably, rapidly, and non-destructively determine spatially defect density are necessary to determine the effects of these defects on device performance.

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

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

4:00pm MC+2D+AP+AS-MoA7 EUV Lithography Mask Cleaning Optimization and TOF SIMS Analysis. Thomas Laursen, S. Novak, SUNY College of Nanoscale Science and Engineering, A. Rastegar, SEMATECH, T. Nakayama, SUNY College of Nanoscale Science and Engineering

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

The surface structures on the EUV mask surface consist of a stack of thin films having thicknesses ranging from 1 to 50 nm. The reflective layer contains 40 bilayers of Mo-Si consisting of 2.7 nm Mo and 4.1 nm Si—ending with a Si layer. This multilayer is usually capped with either a 2.5 nm Ru or in some cases a 2 nm TiO₂ surface film. Metallic films with high extinction coefficient with thicknesses in the range from 35 to 75 nm are deposited as an absorber layer and patterned on Ru-capped multilayer blanks.

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

The interactions of the various segments constituting a cleaning process have been characterized in terms of their effect on film etching and removals as well as film oxidation. In general sulfuric acid - H₂O₂-based treatments caused a severe deterioration of the film structures, whereas the EUVR measurements could be directly related to mask specifications. The TOF-SIMS analysis provided more detailed information on surface contamination and oxidation levels, as well as surface-film integrity.

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

Photovoltaic power source technology is one of the most desirable ways to provide energy for the world of tomorrow. Hence, it is important to understand the surface, electrical and photo-induced properties of these materials in order to enhance their efficiencies. Currently used materials in photovoltaic manufacturing technology are mainly crystalline silicon, CdTe (cadmium telluride), amorphous and nanocrystalline silicon, CIS (copper indium diselenide) and CIGS (copper indium gallium selenide). In this study, we focused only on the silver/copper indium diselenide cells, which contain a CdS layer on top. X-ray photoelectron spectroscopy (XPS) that we used for analysis was modified to apply both an external photo illumination and voltage bias during data acquisition. The first part of the research focuses on the result of photo induced variations in binding energies of elements and the main objective is to understand the different binding energy shifts of each element in the Ag/CulnSe films in both wavelength- and intensity-sensitive fashion under illumination with three different continuous wave lasers. Furthermore, electrical charging properties of CIS/CdS thin film are studied with externally applied electrical square-wave pulses (SQW), so-called Dynamic XPS. Results will be presented with an ultimate aim of better understanding of the roles of defects affecting the performance of CIS devices. This work was supported by a joint NSF-TUBITAK collaborative research project (NSF Grant No: 1312539 TUBITAK Grant No: 212M051).
Composition controlled Cu_{1-x}Zn_{x}O layers have been synthesized on pretreated a-brass followed by ambient oxidation. The pretreatment consists of a vacuum anneal step which effectively depletes the surface of Zn. The depleted Zn specimens were then oxidized at various temperatures ranging from 300°C – 600°C. SEM and XRD result shows the oxide consists of CuO/ZnO film/nanowire composite architecture. The analysis of electronic structure (XPS) and optical properties (PL) shows the formation of Zn containing alloy in the surface region of CuO films. The composition ratio of Cu and Zn were calculated based on XPS survey spectra. In particular, XPS fine spectra revealed that as the oxidation temperature increases, the binding energy of Zn 2p_{3/2} shifts to higher energy, suggesting the possibility of hybridization between the Zn ions and Cu ions.

Photoelectrochemical properties of Cu_{1-x}Zn_{x}O cathodes exhibit robust photocurrent densities (~3 mA/cm²). We suggest the dezincification followed by thermal oxidation provides a better approach for composition tuned nanostructure design and fabrication. These semiconductor nanoarchitectures are excellent candidate materials for fabricating solar energy harvesting photoelectrodes as well as optoelectronic devices.
The chemical functionalization of graphene can alter its electronic, mechanical, and tribological properties. Here we employ atomic force microscopy (AFM) friction measurements to provide a sensitive local probe of the degree of functionalization. These experiments enabled detailed comparison of tribocorrelative reactions between the transfer films or the initial run-in of the film. They also enable experiments difficult by other means. For instance we could directly compare the mechanical barrier to functional group removal by monitoring friction while slowly ramping the applied stress at the maximum reduction rate was ~0.47 ± 0.14 GPa; for fluorinated graphene it was ~0.85 ± 0.27 GPa. Thus, by using the same tip and same substrate we could directly compare the bond strengths between different functional groups and the graphene lattice. This work demonstrates the ability to measure and control the chemistry of single-layer functionalized surfaces at the nanometer scale, and has wide application in tribochemical wear, mechanochemistry, and nanoelectronic device fabrication with chemically tuned optoelectronic properties.

catalytic etching behavior in these two gas environments and provides insights into the catalytic mechanisms involving carbon hydrogenation and carbon dissolution.


Graphene/Semiconductor Schottky devices attracted significant research attention due to wide range of applications from transistor to IR detector [1-2]. Such heterojunctions are also promising for sensing applications due to the molecular adsorption induced Schottky barrier height (SBH) change at the interface, affecting the junction current exponentially in reverse bias, which leads to ultrahigh sensitivity. Graphene/p-Si diode sensor [Device image, Raman spectra and I-V characteristics shown in fig. 1(a), (b) and (c)] has been developed with high bias-dependent sensitivity and low operating power.

Performance enhancement has been demonstrated by fabricating graphene chemiresistor and diode sensor on the same chip. The sensor exhibited 13 times higher sensitivity for NO2 [Fig. 2(a)] and 3 times higher for NH3 [Fig. 2(b)] in ambient condition, while consuming ~500 times less power for same applied voltage. Sensing tunability is achieved by operating the device in reverse bias, tuning the graphene work function and hence the SBH by the applied bias. The sensitivity varied from 268 to 574% for NO2 as the bias magnitude varied from -1 to -8V [Fig. 3(a)] to study the SBH design to detect particular analyte is also possible by careful selection of graphene/Si heterojunction SBF. For example, graphene/p-Si with larger SBH is better NO2 sensor while smaller SBH device has better NH3 sensitivity. The sensing mechanism based on SBH change has been confirmed by capacitance-voltage measurements [Fig. 3(b)]. The SBH decreased by 0.23eV for NO2 exposure while increased by 0.16eV for NH3. Variation in sensitivity with NO2 and NH3 concentration has also been demonstrated (Fig. 4).

Pd and Pt functionalization has been carried out to make the graphene/Si diode [Fig 5] sensitive to H2. Extrapolated SBH from the I-V characteristics, before and after few nm metal decoration, and H2 exposure showed initial SBH decrease after functionalization and subsequent increase in presence of H2, respectively [Fig. 6(a) and (b)]. Compared to graphene chemiresistor, the chemi-diode sensor offers more than one order of magnitude higher bias-dependent sensitivity for both types of functionalization. Similarly, the reverse bias operation also enables low power consumption, tunable sensitivity and detection of H2 down to 1 ppm [Fig. 7(a)] in air which is close to the atmospheric background of 0.6 ppm [3]. Among the two metals, Pd-functionalization always exhibited better sensing response irrespective of the bias voltage [Fig. 7(b)]. Remarkably, for Pd-functionalization, the sensor response showed absolute exponential change with various H2 concentration ranging from 2 to 1000 ppm [Fig. 7(c)].

12:00pm 2D+AS+BI+PS+SS-TuM13 Dielectric Layer Deposition on Graphene Surface by Functionalization with Polar Titanyl Phthalocyanine. Jun Hong Park, I.J. Kwak, K. Sardashti, A.C. Kummel, University of California at San Diego

Several novel designs for beyond CMOS devices have emerged using two-dimensional semiconductors. These devices require deposition of thin insulator layers on 2D semiconductors or between two sheets of 2D semiconductors. However, 2D semiconductors are nearly inert surfaces thereby making uniform nucleation of oxide growth challenging preventing scaling of the insulator thickness. A new technique has been developed to employ a monolayer of ordered metal phthalocyanines (MPC) on 2D semiconductors directly as a monolayer low-k dielectric or as a nucleation layer for oxide growth. The first-order demonstration of the molecular scale observation of formation of O-TiPC mono and bilayers on graphene with UHV scanning tunneling microscopy (STM). O-TiPC monolayers were deposited on HOPG surfaces by organic molecular beam epitaxy. After deposition, O-TiPC forms a monolayer with only few defects, and the crystal structure of monolayer has four-fold symmetry in a 1.4 x 1.4 nm grid. Observation of bright protrusions on each O-TiPC indicates that each O-TiPC in the monolayer is directed outward to vacuum. STM shows the band gap of the monolayer is 1.7 eV and the band gap of the bilayer is 2.3 eV. The monolayer or bilayer can directly be employed for sub-nanometer insulators on 2D semiconductors or between two sheets of 2D semiconductors.

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Tom Scott, University of Bristol, UK, C.A. Stitt, M. Hart, Diamond Light Source Ltd., UK, J. MacFarlane, A. Banos, H. Paraskevoulakos, K. Hallam, University of Bristol, UK

How do you look inside a nuclear waste package without breaking it open?

This question is important when the contained corrosion products are potentially flammable and radioactive. Synchrotron x-rays have been used to perform micro-scale in situ observation and characterization of uranium entrapped in grout; a simulation for some intermediate level waste. Using specially designed analysis cells x-ray tomography and x-ray diffraction have been used to generate both qualitative and quantitative data from a grout encapsulated uranium sample before, and after, deliberately constrained H₂ corrosion. Tomographic reconstructions determined the extent, rates and mechanisms of the reaction occurring by assessing the relative densities between the materials and the volume of corrosion products. The oxidation of uranium in grout was shown to follow the anoxic U + H₂O oxidation regime, and the pore network within the grout was observed to influence the induction period needed for the initiation of uranium hydride formation across the surface of the metal. Powder diffraction analysis identified the corrosion products UO₂ and UH₃, and permitted measurement of corrosion induced stress. Together, x-ray tomography and diffraction provide a means of accurately determining the types and degree of uranium corrosion occurring, thereby offering a future means for studying the reactions occurring in real full-scale waste package systems.

W.J. Siekhaus, W. McLean, of Bristol, UK

Understanding the reactions occurring in real full-scale waste package systems.

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Lumps, Bumps and Pyrophoric Powders - Nuclear Waste Viewed in a New Light

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by UV irradiation has also been implemented to identify the locations of C-C bonds in the lipids, which is highly relevant to the biosynthetic pathways and the function of the lipids. The relative ratios of the unsaturated isomers can now be quantified, as the potential biomarkers for diagnosis of diseased tissues.

9:20am AS+B+VT-TuM5 The Importance of Sample Form and Surface Temperature for Analysis by Ambient Plasma Mass Spectrometry (PADI). Ian Gilmore, T.L. Salter, J. Bunch, National Physical Laboratory, UK

Plasma sources for ambient mass spectrometry are of increasing importance owing to their ability to analyse a wide range of organsics including polymers. Some industrially important molecules are not successfully analysed by electrospray based methods and here plasma methods are making an important contribution. For analysis in industry, it is essential to understand the fundamental mechanisms so that predictions can be made of which classes of materials can and cannot be detected. In this study, we develop a metrology framework to understand the sensitivity of PADI to different substances and material form. We study in detail, the effect of sample temperature on the signal intensity and show that the intensity is proportional to the vapour pressure. Importantly, we also show the sample form, as a film or powder, has a strong effect of sensitivity. For the analysis of thin films at room temperature and using a low plasma power, a vapour pressure of greater than 10^3 Pa is required to achieve a sufficiently good quality spectrum. Using thermal desorption we are able to increase the signal intensity of materials with vapour pressures less than 10^-4 Pa, in thin film form, by between 4 and 7 orders of magnitude. This is achieved by increasing the temperature of the sample up to a maximum of 200 °C. Thermal desorption can also increase the signal intensity for the analysis of powders. Prospects for imaging PADI and sub-micron imaging ambient mass spectrometry imaging will also be discussed.

9:40am AS+B+VT-TuM6 A VAMAS Interlaboratory Study for Desorption Electrospray Ionisation Mass Spectrometry (DESI MS) - Survey of the Measurement Issues. Paulina Rakowska, E. Gardak, F.M. Green, M.P. Seah, T.L. Salter, I.S. Gilmore, National Physical Laboratory, UK

The DESI technique is celebrating a decade of application since its innovation in 2004. There has been significant progress in understanding its fundamentals and a rapid expansion in the applications, covering a diverse range of science and technologies. For wider uptake in industry, measurements need to be repeatable and constant. It is especially important to test that methods are transferable between different instrument designs and that analytical procedures are clear. This requires the development of a metrological infrastructure. Interlaboratory studies are an effective route to making an important contribution. For analysis in industry, it is essential to understand the fundamental mechanisms so that predictions can be made of which classes of materials can and cannot be detected. In this study, we develop a metrology framework to understand the sensitivity of PADI to different substances and material form. We study in detail, the effect of sample temperature on the signal intensity and show that the intensity is proportional to the vapour pressure. Importantly, we also show the sample form, as a film or powder, has a strong effect of sensitivity. For the analysis of thin films at room temperature and using a low plasma power, a vapour pressure of greater than 10^3 Pa is required to achieve a sufficiently good quality spectrum. Using thermal desorption we are able to increase the signal intensity of materials with vapour pressures less than 10^-4 Pa, in thin film form, by between 4 and 7 orders of magnitude. This is achieved by increasing the temperature of the sample up to a maximum of 200 °C. Thermal desorption can also increase the signal intensity for the analysis of powders. Prospects for imaging PADI and sub-micron imaging ambient mass spectrometry imaging will also be discussed.

11:40am AS+B+VT-TuM12 Transporting Ions from Ambient Pressure into Vacuum for Lab-based and Mobile Mass Spectrometers. Mitch Wells, FLIR Mass Spectrometry

The proliferation of Atmospheric Pressure Ionization (API) sources for mass spectrometry (MS) has expanded the applicability of the MS analysis technique to a wide range of chemical and biological challenges, to the extent that the 2002 Nobel Prize in Chemistry was awarded to John Fenn and Koichi Tanaka for their development of Electrospray Ionization (ESI) and Matrix-assisted Laser Desorption Ionization (MALDI), respectively. Furthermore, recent developments in a specific category of API, referred to as Direct Analysis in Real Time (DART) or similar terminology, have all been examined with AI, to name just a relatively few examples. All API techniques have in common the need to transport ions from atmospheric pressure into the high vacuum of the mass spectrometer - typically <10^-5 Torr (<1 mPa). Various ion sampling and transport mechanisms are used to transfer ions through differentially-pumped vacuum stages to the mass analyzer. In all cases, significant losses at each stage mean that only a very small fraction (<~1%) of the ions generated from a sample are actually analyzed. The situation is even worse for systems that are intended to be used in mobile or field labs, where space and power are at a premium and large pumping systems are therefore not acceptable. This talk will briefly review AI techniques to illustrate their value in analytical chemistry (including biological, clinical, and forensic analysis), and will then describe means by which ions are transported from atmosphere into vacuum, with the hope of stimulating dialog with the vacuum community about ways and means that this process could be improved, especially for small, rugged instruments designed for outside-the-lab use.

Biomaterial Interfaces

Room: 317 - Session BI+AS+MN+NS-TuM

Biosensors

Moderator: Graham Leggett, University of Sheffield


We present a real-time biofilm monitoring device based on inductive-capacitive (LC) sensing principles. Bacterial biofilms cause severe infectious diseases and environmental contamination. The bacterial biofilm's complex structure and composition, as well as its ability to exchange genetic information, result in a high tolerance for antimicrobial agents. As a result, established biofilm control technologies using biomedical devices, such as catheters, are difficult to treat. Traditional antibiotic therapies for biofilm infections only require doses 500-5000 times larger than for non-biofilm infections [1]. Moreover, biofilm growth in environmental and industrial facilities causes contamination and corrosion of equipment due to the toxins generated by biofilms. Therefore, early detection of biofilm growth is critical to facilitate treatment of severe infections and prevent equipment contamination.
In this work, an LC sensor was fabricated using conventional lithography and metal deposition via E-beam evaporation (Cr/Au, 15 nm/200 nm) (Figure 2). The resonant frequency of the sensor was approximately 16 MHz in air at room temperature. A device sensitivity of 1140 Hz/dielectric material was demonstrated using a known dielectric material (deionized water) in air at room temperature. A device sensitivity of 1140 Hz/dielectric material was demonstrated using a known dielectric material (deionized water).

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In this work, an artificial approach for enhanced microbial biocatalysis was explored along with study of the parameters promoting bacterial electrocatalysis. This approach consisted of artificial modification of electrode surfaces having, as a result, different surface chemistries. Mixed bacterial culture development, biofilm growth and electrochemical performance have been studied. Smooth gold surfaces were modified with organic thiol to form self-assembled monolayers (SAMs) with various functional groups (CH3, -OH, -N(CH3), and -COOH).

Power curves and single electrode polarization curves have been taken to evaluate the performance of the MFC as a whole and of the electrodes separately. XPS analysis of electrodes was used to study the effect of chemistry on the performance. Confocal and SEM microscopy was used to study the bacteria biomass and biofilm development was tracked over time.

Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM+SE-TuM

Fuel Formation and Thermal Transport
Moderator: Michael Filler, Georgia Institute of Technology
8:00am EN+AS+EM+SE-TuM1 Unraveling Thermodynamic and Kinetic Factors in Solar-Thermochemical Fuel Production. Sossina Haile, California Institute of Technology.

Perhaps the greatest challenge facing our planet is sustainable energy. Given the vast solar energy resource base available to modern society, key to addressing this challenge is the conversion of solar energy into a storable form suitable for on-demand utilization. So emerges the concept of ‘Solar Fuels’. Amongst many approaches currently pursued to generate solar fuels, the thermochromic dissociation of water splitting is particularly attractive. It provides the benefits of full utilization of the solar spectrum and inherent temporal separation of hydrogen and oxygen gases. In recognition of these advantages, numerous multi-step cycles have been considered over the past several decades. Recently, two-step cycles making use of nonstoichiometric oxides have received attention because of the simplicity of their implementation. The approach relies on the large oxygen nonstoichiometry change that the material undergoes in response to variations in oxygen partial pressure (pO2) and temperature (T). Specifically, upon exposure to high temperatures ceria undergoes reduction without change in crystalline phase to release oxygen. On cooling in the presence of H2O (or CO2), the oxide is reoxidized, releasing H2 (or CO). The success of the method relies not only on favorable thermodynamics but also on facile kinetics, both in terms of surface reaction rates and bulk diffusion coefficient. Accordingly, we have undertaken a comprehensive study of ceria and its doped derivatives to assess both the equilibrium redox behavior by thermogravimetric methods and the kinetic response by conductivity relaxation methods. We find, for example, that introduction of Zr strongly increases the absolute non-stoichiometry of ceria, but at a penalty in terms of the sensitivity of the nonstoichiometry change to changes in environmental conditions and in terms of bulk diffusion. In another example, we find that the relaxation behavior of Sm-doped ceria is substantially more rapid than that of both undoped and Zr-doped ceria, a result that is tentatively assigned to differences in species mobilities. The implications of these fundamental differences in material properties for thermochemical fuel production are discussed.

8:40am EN+AS+EM+SE-TuM3 Controlling Catalysis on Metal Nanoparticles by Direct Photoexcitation of Adsorbate-Metal Bonds. M.J. Kale, T. Avanesian, University of California, Riverside. H. Xin, J. Yan, SLAC National Accelerator Laboratory.

Heterogeneous photocatalysis is typically assumed to occur via photon absorption by a solid-state photocatalyst (only the photocatalyst electronic states are involved in photon absorption) followed by charge carrier diffusion through the photocatalyst bulk and subsequent transfer to adsorbates. This process of energetic charge carrier generation and transfer results in wavelength dependent quantum efficiencies that strictly follow the absorption spectrum of the solid-state photocatalysts, regardless of the chemical transformation. The substrate mediated photocatalysis mediated photocatalysis absorption process inhibits approaches to control reaction selectivity by matching photon excitation wavelengths to bond specific electronic transitions, as typically done in molecular systems.

Here, we show that strong chemisorption bonds formed between CO and Pt metal surfaces can be activated with visible photons to drive catalysis through direct, resonant photoexcitation of hybridized Pt-CO states. This is enabled as the dominant photoexcitation mechanism (over substrate mediated photoexcitation) driving catalysis by using 5-nm nanoparticle Pt nanoparticle catalysts, where high surface area to volume ratios force photon absorption onto surface metal atoms. The direct photoexcitation process is observed to be significantly more efficient for driving photooxidation than the direct photooxidation process when the energy of exciting photons is resonant with adsorbate specific electronic transitions involving hybridized metal-adsorbate states. It is also demonstrated that resonant photoexcitation of Pt-CO bonds on sub-5-nanometer Pt nanoparticles by visible light significantly enhances selectivity towards CO2 over H2O production, in the selective oxidation of CO by O2 in an H2 rich environment (also known as the thermal CO oxidation). These results open new avenues to control catalytic reaction selectivity on sub-5 nm catalytic particles by resonant photoexcitation of adsorbate-specific electronic transitions involving hybridized metal and adsorbate states. It is expected that the development of insights into resonant electronic transitions between hybridized metal-adsorbate states should allow rational control of catalytic selectivity that cannot be achieved exclusively with thermal energy input.
insight to molecular junctions and how this insight translates to design principles for polymer and hybrid thermoelectrics.

The amount of thermal energy rejected as waste heat from industrial processes in the United States has been estimated at 32 quardrillion BTU per year, with an associated emission of 1,680 million metric tons of carbon dioxide. The ability to cost-effectively convert a portion of this thermal energy into useful electrical energy could improve energy efficiency, reduce operating costs, and decrease CO2 emissions. Waste heat is typically categorized by temperature as high-grade (650°C and above), medium-grade (232°C to 650°C, and low-grade (232°C and below). In order to improve the thermal-to-electrical conversion efficiency of medium-grade waste heat, RTI has combined two different materials to form a high figure-of-merit, hybrid thermoelectric (TE) device. Recently-developed enhanced “TAGS-85”, or e-TAGS, was employed as the p-leg, while the n leg was comprised of improved half-Heusler (HH) material. This hybrid material pair provides a high ZT, lead-free TE material solution for waste heat recovery for use in vehicle or industrial platforms. The improved HH material employs two novel techniques to reduce thermal conductivity: (1) high-energy milling, and (2) addition of coherents inclusions. Single n/p-couples were produced that achieved a 9.2% thermal to electric power conversion efficiency for $T_{\text{hot}} = 559^\circ\text{C}$ and $\Delta T = 523K$. This is a significant efficiency improvement at a lower hot side temperature with the hybrid e-TAGS/HH single couple over the performance of a conventional, all HH efficiency improvement at a lower hot side temperature with the hybrid e-TAGS/HH single couple over the performance of a conventional, all HH couple. By optimizing the cross sectional areas of the pellets for equal heat flow, the resulting asymmetric couple achieved a conversion efficiency of 10.5% at $T_{\text{hot}} = 537^\circ\text{C}$ and $\Delta T = 497^\circ\text{C}$. A 49-couple hybrid module using HH materials paired with e-TAGS and operated with $T_{\text{hot}}$ up to 600°C reached a maximum efficiency of 10%. The improved module efficiency is believed to be due to both improved materials and optimized cross-sectional area ratios between the n- and p-elements. We will also discuss additional advances in thermal to electric power conversion using multi-stage modules.

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

Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)

Moderator: Franklin (Feng) Tao, University of Notre Dame

8:00am IS+AS+MC+SS-TuM1 The ISSIS Facility at BESSY II and Beyond: The Application of Near Ambient Pressure X-ray Electron Spectroscopy in the Surface Characterization of Technical Catalysts, Michael H"avecker, Helmholtz-Zentrum Berlin f"ur Materialien und Energie/Elektronenspeicherring BESSY II, Germany. Ch. Heine, M. Eichelbaum, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, F. Rosowski, BasCat, UnCat-BASF JointLab, Germany. A. Trunshcke, R. Sch"ogl, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany.

INVITED

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

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

References


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


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

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

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

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

Photoelectron spectroscopy went through a revolution in the 1990’s, with the development of parallel angular detection using 2D detectors, a development that VG Scienta is proud to have contributed to. The possibility of simultaneous recording of Angular Resolved PES (ARPES) spectra enables not only band structure measurements, but also x-ray
photoelectron diffraction (XPD), depth profiling and standing wave spectroscopy. Recent examples within APPES will be given. The use of 2D detectors to record parallel spatially resolved spectra is a related technique. Here we will show experimental results as well as very recent instrument developments to obtain world leading spatial resolution at ambient conditions.

The combination of APPES and Hard X-ray Photoelectron Spectroscopy (HAXPES) has recently become an established technique. We will show results of the use of this combination to decrease inelastic scattering of the photoelectrons as well as to tailor the probing depth of advanced systems. In APPES, more than in UHV PES, instrument usability and sample handling is a key to successful measurements. VG Scienta has developed several complete system offerings to maximize productivity in the lab. These will be discussed on a conceptual level, as well as in some detail.

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

It is critical to develop a catalyst made of earth-abundant elements highly active for a complete combustion of CH₄ at a relatively low temperature for catalytically transforming CH₄ to electrical energy in power plant. The currently available catalysts with high activity consist of precious metal nanoparticles supported on rare earth oxides. Their high cost limits the application of these catalysts at industrial scale. Here we report a new catalyst, early transition metal oxide-based mixed oxide only consisting of earth-abundant elements which can completely combust CH₄ at 350°C at a gas hourly space velocity of 240,000 ml 0.5% CH₄ on 1 gram in one hour. This higher activity or even higher catalytic performance results from the integration of Ni cations and surface lattice oxygen atoms at the atomic scale. With such an integration, the carbon atom dissociated from CH₄ can bond with its neighboring surface oxygen atoms to form an intermediate of CO₂ and then desorb.

In-situ studies of catalyst surface using AP-XPS and monitoring of products formed from isotope-labeled catalysts show that (1) molecules O₂ dissociate on surface oxygen vacancies, (2) half of the dissociated oxygen atoms remain in oxygen vacancies, (3) the other half of dissociated oxygen atoms directly bond with hydrogen atoms dissociated from CH₄ to form OH and then H₂O molecules, (4) CH₃ successively dissociates on Ni cations to form CH₃ (n=3, 2, 1, 0), (5) carbon atoms bind to two surface lattice oxygen atoms nearby to form a carbonates species, O-C-O intermediate, and then desorb. The mixed cations and surface lattice oxygen atoms in this mixed oxide at atomic level makes the formation of an O-C-O intermediate at a mild temperature since a spillover of dissociated species is not necessary.

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

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


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

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

We have designed and characterized electron transparent windows for environmental cells dedicated for ambient pressure XPS spectroscopy and electron microscopy of liquid and gaseous samples. These windows made of single or multi-layered graphene have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons what allow to conduct interfaccial spectroscopy of fully hydrated samples without differential pumping setup. In addition, these membranes are thermally and chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in graphene fabrication and transfer protocols we demonstrate the capability to perform in situ XPS and electron microscopy studies of the electrochemical processes taking place at liquid electrolyte-solid interface.


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

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

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

While Surface Science provided useful insights into a variety of materials of interest for catalysis, its contribution to the understanding of zeolites and clays has been limited. This was mainly due to the lack of suitable well-defined surfaces that successfully mimic the properties of these important materials while allowing its analysis using the vast toolkit of surface science. This talk will describe an aluminosilicate ultra-thin (~ 0.5 nm) film that was recently synthesized, which provides a good model system for zeolites and clays. It consists of a bilayer structure, as shown in the figure, and it counts with bridging hydroxyl groups. The latter are the active sites of these ternary solutions is important for predicting reactivity at aqueous surfaces.

References
**Surface Science**

**Room:** 309 - Session SS+AS+EN-TuM

**Synthesis, Structure and Characterization of Oxides**

**Moderator:** Andrew Gellman, Carnegie Mellon University

8:00am SS+AS+EN-TuM1 Coexisting Accessible Surface Phases on BaTiO₃ (001). **Erie Morales, J.M. Martinez,** University of Pennsylvania, **W.A. Saidi,** University of Pittsburgh, **A.M. Rappap, D.A. Bonnell,** University of Pennsylvania

Novel ferroelectric BaTiO₃ applications ranging from sensors to nanogenerators require a detailed understanding of atomic interactions at surfaces. Single crystals provide a platform that allows the exploitation of surface physical and chemical properties that can be readily transferred to other ABO₃ perovskite structures. The processes that result in the atomic and electronic structures of surfaces in tandem with details of surface reactivity are necessary steps towards an understanding of BaTiO₃. Here we demonstrate that two surface reconstruction phases can coexist on a surface and explain the stability of the surface with a quantitative comparison of thermodynamic and kinetic considerations. Specifically, scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) of atomically resolved c(2x2) and c(4x4) reconstructions on BaTiO₃(100) are compared with density functional theory models to determine the structures of the phases. First principles calculations are also used to examine the thermodynamic stability of the phases and the reaction pathways to both the stable and meta-stable structures. We also show how the atomic structures of the ferroelectric properties of BaTiO₃ lead to polarization dependent surface reactions and recent results based on poling at atomic level will be discussed.

8:20am SS+AS+EN-TuM2 Oxidation and Chemical Reactivity of TbOₓ Thin Films on Pt(111). **W. Cartus, R. Rai, A. Sathe,** University of Florida, **A. Schafer,** University of Bremen, Germany, **Jason Weaver,** University of Florida

Rare earth oxides (REOs) exhibit favorable catalytic performance for a diverse set of chemical transformations, including both partial and complete oxidation reactions. In this talk, I will discuss our recent investigations of the growth, oxidation and chemical reactivity of TbOₓ(111) thin films on Pt(111), and make comparisons with results for SmOₓ(111) films grown on the same substrate. Bulk terbia and samaria represent examples of REOs that are reducible vs. effectively irreducible, respectively. From low energy electron diffraction and scanning tunneling microscopy, we find that samaria and terbia grow as high quality thin films on Pt(111) during deposition in ultrahigh vacuum. Both oxides develop in the LnOₓ stoichiometry and adopt an oxygen-deficient fluorite structure wherein the metal cations form a hexagonal lattice in registry with the Pt(111) substrate, while oxygen is in a disordered arrangement. Contrary to what has been observed for CeO₂(111), lines and simple coincidence superstructures are observed. The ceria overlayer grows essentially 2-D, but displays a peculiar nanostripe pattern, with varying periodicities ranging from 4-8 nm and a corrugation amplitude of 0.2-0.3 nm. This nanostripe pattern is due to a topographic modulation of the overlayer caused by the frustration of overlayer-substrate bonding as a result of the epitaxial mismatch at the ceria film surface. Detailed topographic and atomic resolution images of the ceria lattice in the transition region between dark (low) and bright (high) stripes, which gives rise to periodic regions of anisotropic lattice strain - so-called "lattice strain defects". It is speculated that these lattice strain defects may support particular chemical reactivity.

Work supported by the ERC Advanced Grant "SEPON" and by the COST Action CM1104

9:00am SS+AS+EN-TuM5 Ceria on Cu(110): Formation of Nanostripe Strain Defects. **L. Ma, N. Doudin, S. Surney, Falko Netzer,** Karlf-Franzens University, Austria

The growth morphology and atomic geometry of ceria nanostructures on Cu(110) have been investigated by STM, LEED and XPS. Ceria grows epitaxially in a two-dimensional (2-D) hexagonal layer, which is associated with a CeO₂(111)-type trilayer structure forming a (3x11) coincidence lattice. An important experimental parameter is the oxygen pressure during growth: it influences the stoichiometry of the ceria overlayer as well as the Cu surface oxide phase, which coexists with the ceria for coverages below the full monolayer. For oxygen pressures in excess of 10⁻⁴ mbar, stoichiometric CeO₂ and coexisting Cu-O(Ox)₂ surface oxide is formed, whereas for lower oxygen pressures, in the 10⁻⁵ mbar range, slightly substoichiometric ceria small CeO₂(2x1) islands coexist with the Cu surface oxide. STM images and CeO₂ islands are observed. The ceria overlayers grows essentially 2-D, but displays a peculiar nanostripe pattern, with varying periodicities ranging from 4-8 nm and a corrugation amplitude of 0.2-0.3 nm. This nanostripe pattern is due to a topographic modulation of the overlayer caused by the frustration of overlayer-substrate bonding as a result of the epitaxial mismatch at the ceria film surface. Detailed topographic and atomic resolution images of the ceria lattice in the transition region between dark (low) and bright (high) stripes, which gives rise to periodic regions of anisotropic lattice strain - so-called "lattice strain defects". It is speculated that these lattice strain defects may support particular chemical reactivity.

9:40am SS+AS+EN-TuM6 Design Rules for Stabilizing Polar Metal Oxide Surfaces: Adsorption of O₂ on Zn-rich Polar ZnO(0001). **Ming Li,** **Gorai, E. Ertelkin, E.G. Seebauer,** University of Illinois at Urbana-Champaign

For oxide semiconductors with appreciable ionic character, undercoordination of the surface atoms leads to thermodynamic instability that is typically restored by reconstructions, faceting, or extensive surface defect creation. Developing design rules for stabilizing polar metal oxide surfaces that avoid these phenomena could offer novel protocols for applications such as improved nanostructure growth and design of photocatalytic heterostructures. The present work describes calculations by density functional theory for Zn-rich polar ZnO(0001) which demonstrate that stabilization via chemisorption of O₂ together with vacancy formation is energetically as favorable as stabilization by vacancies alone. The stabilization mechanism including adsorption is so effective that it promotes O₂ adsorption to an extent that is not possible on non-polar ZnO. Experimental evidence for such stabilization behavior is presented based on measurements of O₂ adsorption on polar ZnO(0001) via the optical
modulation technique of photoreflectance. The measured isotherms yield a sizable adsorption enthalpy of adsorption near 1.8eV, confirming a strong interaction with the polar surface.

11:00am SS+AS+EN-TuM10 The Growth of Catalytic Thin Films on a Polar Substrate: Cr$_2$O$_3$ on ZnO (0001) and ZnO (000-1), Xiaodong Zhu, Yale University

Zinc oxide is a wurtzite-structured polar crystal with dramatic polarization direction-dependent surface chemistry. Meanwhile, chromium III oxide is a non-polar material catalytically active for a number of industrial chemical reactions, most notably dehydrogenation. Therefore, the Cr$_2$O$_3$/ZnO system has been chosen to demonstrate how the polarization direction of a substrate can be exploited to tailor the surface properties of catalytically active non-polar thin films. Photoelectron spectroscopy and electron diffraction have been performed to determine the growth mode as well as the film quality. The growth is 2D; however, the films appear initially disordered on both positive and negatively poled substrates. On both substrates the order was observed to improve with thickness. Small band offsets between Cr$_2$O$_3$ and oppositely poled substrates were observed that were consistent with charge compensation at the Cr$_2$O$_3$/ZnO interface. No obvious change in the oxidation state of the chromium was seen and so it is assumed that the charge compensation at the interface only involves Zn and/or O. The offset between the Cr peaks on positively and negatively poled substrates was observed in the initial growth stages but then decayed with film thickness, suggesting that the compensating charges at the interface may migrate to the film surface. Valence band spectra were analyzed to characterize the thin film. Surface chemical behavior of Cr$_2$O$_3$ on the two zinc oxide surfaces is being characterized to determine how significantly the polar interface impacts the surface properties of thin supported layers.

11:40am SS+AS+EN-TuM12 Chemical Characterization of Elements in Oxides using X-ray Satellite Lines, Terrence Jach, National Institute of Standards and Technology (NIST)

X-ray satellite lines come about in x-ray fluorescence spectroscopy as a result of shake-off events in the excitation process. The ratio of their intensities has been shown to be a sensitive function of their oxidation states. We are able to observe the K satellite lines in the x-ray spectra of oxides and glasses, excited by the beam of an electron microscope and detected by a high resolution x-ray microcalorimeter detector. The results show surprising departures from the expected states of some metal elements that we expect to be fully oxidized. The satellite ratio is a way of determining the chemical environment of insulators without charging or ultra-high vacuum.


The intrinsic point defects associated with oxygen vacancies and Ti$^{3+}$ ions play a crucial role in the usage of titanium dioxide (TiO$_2$) in various technological applications including catalysis and photochemistry. It is well known that the interactions between H atoms and surface oxygen in TiO$_2$ lead to the formation of Ti$^{3+}$ ions at elevated temperatures. However, the Ti$^{3+}$ ion formation and accumulation as a function of elevated temperatures in UHV conditions during hydrogen diffusion in TiO$_2$ is not well understood. In this study, we have used ion implantation method to incorporate hydrogen in single crystal TiO$_2$ (110) samples and investigated the behavior of point defects in both pure and hydrogen implanted TiO$_2$ as a function of elevated temperatures using Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), x-ray photoelectron spectroscopy (XPS) and ultra violet photoemission spectroscopy (UPS). TiO$_2$ single crystals were implanted with 40 keV hydrogen ions at room temperature with ion fluences of $1 \times 10^{15}$, $1 \times 10^{16}$ and $1 \times 10^{17}$ atoms/cm$^2$. Samples were isochronally annealed in vacuum for 30 minutes at each temperature up to 1100K and hydrogen and Ti$^{3+}$ defects were quantified. Hydrogen depth profile measurements obtained from $1 \times 10^{17}$ atoms/cm$^2$ implanted sample reveal that hydrogen diffused towards the surface at lower temperatures and it slowly diffuses out from the samples at higher temperatures. XPS and UPS measurements from the hydrogen implanted samples show significantly higher Ti$^{3+}$ defects in comparison to pure TiO$_2$ at these temperatures under UHV conditions. These defects reach a maximum around 880 K in which almost all hydrogen was removed from the sample. When the implanted sample further annealed to high temperatures, the amount of Ti$^{3+}$ in hydrogen implanted samples started to decrease and reaches the values from the pure TiO$_2$ samples around 1100K.
2D Materials Focus Topic

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

2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Manish Chhowalla, Rutgers University

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

Because of their weak Van der Waals interlayer bonding transition-metal dichalcogenide (TMDC) semiconductors can be fabricated into atomically thin two-dimensional (2D) crystals with substantial ~ 1-2 eV bandgaps. As one example, monolayer MoS2 consists of a single layer of Mo atoms sandwiched between two layers of S atoms in a trigonal prismatic structure. The TMDC 2D system has attracted great attention because of its distinctive electronic and optical properties, such as (i) a transition from indirect-to-direct band gap in going from the multilayer to monolayer crystal due to a missing interlayer interaction in monolayer form and (ii) strong spin-orbit-coupling-induced split valence bands, i.e. 100’s of meV, due to broken inversion symmetry, which makes TMDCs interesting for spin-physics and devices. Both properties have been predicted with density functional theory (DFT) calculations and indirectly demonstrated using photoluminescence and Raman spectroscopy.

Recently we have made a series of direct observations of the thickness-dependent electronic-band and crystal structure of TMDCs of both exfoliated and CVD grown samples. Because of the relatively modest sample sizes we have used micrometer-scale, angle-resolved photo-emission spectroscopy (micro-ARPES) of both the exfoliated and chemical-vapor-deposition-grown crystals; these measurements provide direct evidence for the shifting of the valence band maximum from gamma bar (Brillouin zone center) to kappabar (Brillouin zone corner), as the sample thickness decreased from bulk to monolayer. Our initial results were with MoS2 and are described in a preliminary way in Refs 1 and 2. Our TMDC experimental results are compared with rigorous DFT calculations of both the bands and the UV transitions matrix elements. The results show an evolution in band structure, which is consistent with an indirect-to-direct bandgap transition in going from few-layer to monolayer TMDC and can be attributed to changes in quantum confinement as the number of layer decreases. Our microARPES and, subsequently, higher resolution nanospectroscopy data provide clear measurements of the hole effective mass, the strain present in the monolayer crystal films, and the valence-band spin-orbit splitting. Our results explain the low hole mobility of monolayer MoS2 compared to thicker MoS2 and show clearly the strong orbit split energies. Our results, using nanoLEED and LEEM also provide insight into the structure and defects in monolayer films. Experiments using K-doping of single-crystal samples and resulting level shifts are also described.


3:00pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA3 X-ray Photoemission and Electron Energy Loss Spectroscopy Investigation of the Band Gap and Band Alignment for h-BN and MoS2 Materials and Interfaces, Benjamin French, J. Brockman, M. French, M. Kahn, J.D. Bielefeld, S.W. King, Intel Corporation, E. Bersch, G. Borsuker, SEMATECH, J. DiStefano, Y.C. Lin, J.A. Robinson, Penn State University

Hexagonal boron nitride (h-BN) and molybdenum disulfide (MoS2) are two dichalcogenide (TMDC) semiconductors that have shown interesting electronic properties and applications. Due to a wide band gap (~ 6 eV), close lattice matching (~ 2%) and atomic planarity, hexagonal boron nitride (h-BN) is of primary interest as a potential substrate and gate dielectric in graphene channel transistor devices. In contrast, MoS2 is a 2D semiconducting material with a band gap of ~ 1.8 eV that is attractive as a possible complement or alternative to graphene for nano-electronic devices requiring a large band gap. A key property for the success of both h-BN and MoS2 in such devices is the interfacial band alignment with graphene, the gate contact metallization and the surrounding insulating dielectric materials. In this regard, we have utilized x-ray photoelectron spectroscopy (XPS) to determine the Schottky barrier and valence band offsets present at the interfaces between plasma enhanced chemically vapor deposited amorphous h-BN:H and chemically vapor deposited MoS2. In combination, we have utilized reflection electron energy loss spectroscopy (REELS) to investigate the band gap of both h-BN and MoS2 materials to deduce the conduction band alignment. We show that in many instances the valence and conduction band offsets are significant and favorable for MoS2/h-BN transistor devices.

Tuesday Afternoon, November 11, 2014

3:20pm 2D+AS+HI+MC+NS+PS+SP+SS-TuA4 STM/STS Characterization of MoS2 Monolayers and Nanostructures, A. Mills, C. Chen, Virginia Tech, Y. Yu, L. Cao, North Carolina State University, Chenggang Tao, Virginia Tech

Atomically thin molybdenum disulfide (MoS2) and nanostructures have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. Especially, monolayer MoS2, an atomically thin semiconductor with a direct band gap, as opposed to an indirect band gap in bulk MoS2, has been demonstrated as field effect transistors, optoelectronic devices and chemical sensors. In our experimental study, Monolayer MoS2 and MoS2 triangular nanostructures are synthesized through a self-limiting chemical vapor deposition (CVD) approach. The precursor materials, MoCl5 and sulfur, react at low temperatures to produce MoS2 that spontaneously precipitate onto substrates to yield MoS2 films and triangular nanostructures. Using scanning tunneling microscopy (STM), we have investigated the structural and electronic properties of monolayer MoS2 grown on glassy carbon and triangular MoS2 nanostructures on highly ordered pyrolytic graphite (HOPG). We will also discuss our scanning tunneling spectroscopy (STS) measurements on these structures.

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

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

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

Hexagonal boron nitride (h-BN) has grown into prominence as a dielectric for graphene heterostructures. h-BN and graphene have been grown using chemical vapor deposition on various transition metal substrates. Compared to graphene, the morphology of CVD-grown boron nitride on Cu has not been as widely studied. Here, we present a systematic study of the morphology of hexagonal boron nitride (h-BN) grown on polycrystalline Cu foils by chemical vapor deposition. The growth of h-BN is performed at ~1000°C in atmospheric pressure CVD with Ammonia Borane (H3NBH3) as the precursor. The copper foils, used as catalytic substrates, are thermally annealed at ~1030°C for ~5 hours prior to growth and cooled slowly following growth termination. We utilized Ultra-high vacuum Scanning Tunneling Microscopy (STM), ambient AFM and SEM to assess the morphology of the CVD grown h-BN films. Highly symmetric single
crystallites of h-BN are observed for sub-monolayer growth, in agreement with recent reports. We consistently observe a corrugated topographic structure within the h-BN crystallites which is distinctly different from the surrounding copper surface, and this is consistently seen in STM, AFM, and high-resolution SEM. Our aim is to understand the nature of this difference and whether it might be due to effects of differential thermal contraction between h-BN and copper. However, complications arise due to possible changes in the copper substrate topography post-growth due to surface oxidation of the copper. Preliminary results with lateral force microscopy (LFM, frictional mode) show that these corrugations are unidirectional in a single Cu grain irrespective of the orientation of the h-BN crystal and generate frictional forces 200% greater than on the surrounding copper surface, reminiscent of earlier reports of unique frictional behavior in atomically-thin membranes [1]. STM and AFM are also used to study the twin boundaries of h-BN. Preliminary STM observations indicate that merging h-BN crystals consistently have a gap of about 5 nm between them. The results of this study are independent of small variations of growth conditions.

References:


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

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

5:40pm 2D+AS+Hi+MC+NS+SP+SP+SS-TuA11 Novel Materials Properties at Atomically Thin Limit, Zhi-Xuan Shen, Stanford University

In this talk, I will discuss recent progress in uncovering novel materials properties at ultra-thin limit, with focus on mono-unit-cell superconductor FeSe and semiconductor MoS2 respectively. The observation of a large superconducting-like energy gap which opens at temperatures up to 65 K in single unit cell (1UC) thick selendine films on SrTiO3(FeSe/STO) has generated tremendous interest. A challenge is to understand the cause of enhanced Cooper pairing strength in this system, and possibly increase superconducting Tc. In this talk, we show angle-resolved photoemission spectroscopy, mutual inductance, and other measurements on 1UC and multi-UC thick FeSe films grown on Nb-doped SrTiO3. Our data provide clear evidence for strong cross-interface electron-phonon coupling in single UC, raising the possibility that large pairing gaps are caused by the strong coupling between the FeSe electrons and certain collective modes of SrTiO3. This suggests a pathway of "integrated functional components" approach to boost superconducting properties.

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

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

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

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

The most widely used industrial processes for modifying the surfaces of polymer films are flame and corona (dielectric barrier discharge) treatments. While both of these processes oxidize a thin surface region of the treated films, there are significant differences between the surfaces generated by the two surface-oxidation processes. A principal difference between corona and flame treatments is the likelihood to form water-soluble low-molecular-weight oxidized material (LMWOM). LMWOM is formed by the simultaneous oxidation and chain scission of a polymer material. LMWOM is an important surface characteristic that has a large effect on the wetting and adhesion properties of polymer surfaces. LMWOM can be investigated by a number of surface analytical techniques, including x-ray photoelectron spectroscopy (XPS or ESCA), static secondary ion mass spectrometry (SIMS), atomic force microscopy (AFM), and contact angle measurements. This presentation will demonstrate how surface analysis enables the detection and detailed characterization of the LMWOM formed by the flame and corona treatment of polypropylene (PP) film surfaces. The mechanism of LMWOM formation can be then determined from these analytical results when coupled with an understanding of the bulk photo-and-thermal degradation of PP materials.

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

Modifications of fabrics are becoming more important for a wide variety of applications. For example, loading TiO2 onto cotton can improve many of the material properties, such as anti-bacterial effects, UV protection, and stain resistance. The conformity of these modifications across sample surfaces are an important part of the application process. By using XPS in addition to other techniques, surface concentration and conformity can be determined and deduced whether the samples have met certain criteria, and how the uniformity, of lack thereof, can affect the desired outcome of the modifications.

This presentation will look at the possibility of in situ photoreduction of Ag ions on the surface of TiO2 nanoparticles to create "active fabrics", and will utilise XPS imaging to determine whether deposition on the surface of different fabrics has been successful.

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

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

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

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

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

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

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

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

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

The knowledge of the tin oxidation process is important for the development corrosion-free coatings and the engineering of alloys and compounds with specific functional properties. Tin, pure and well controlled oxidized samples were characterized by X-ray photoelectron spectroscopy (XPS). All samples were prepared on Si (100) substrates with RCA treatment before Sn deposition. The thickness of the Sn layer was approximately 100 Å as measured by a thickness monitor. The pure Sn sample was measured without ambient exposure. The oxidized samples were obtained by exposing pure Sn samples to pure oxygen at a pressure of 1x10⁻³ Torr. Three different exposure times were used: 10, 180 and 1200 seconds. To fit XPS spectra, traditional and novel method (using a double-Lorentzian) were employed to calculate thickness and composition of the oxide layer. High resolution transmission electron microscopy measurements were performed to validate calculations. Structural parameters obtained with different XPS data fitting approaches were compared, showing a clear advantage of the double-Lorentzian method in the understanding of the initial stages of tin oxidation.

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

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

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


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


Development in nanoscale engineering has enabled bioelectronics that can mimic and/or interact with the biological systems. Lipid bilayer functionalized Si nanowires act as the interface for the construction of bio-nano electronic devices. These biomimetic lipid bilayers serve as a general host matrix for bio-functional components such as membrane proteins. Though meaningful technological advancements have been made, critical questions still remain, in particular on structural characteristics of lipid bilayers at the interface with inorganic nanomaterials. Small-angle and wide-angle x-ray scattering (SAXS/WAXS) techniques are used to investigate self-organizations of dioleoyl-phosphatidylcholine (DOPC) lipid bilayers on Si nanowires. Critical structural parameters of the lipid bilayers (lamellarity, bilayer thickness and packing order of lipid molecules) are obtained through analyzing SAXS- derived Electron Density Profile (EDP). A decrease in bilayer thickness and a packing disorder of the lipid head groups in adjacent to supported Si nanowires have been observed upon coating on Si nanowires. Furthermore, effects on the packing order of lipid hydrocarbon tails induced by the incorporations of proteins or carbon nanotubes into lipid bilayers (served as natural or artificial ion channels, respectively) have been identified and characterized. The results shed light on a number of unresolved questions that are crucial for the comprehensive understanding this class of materials.
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Biomaterial Interfaces
Room: 317 - Session BI+AS-TuA

Characterization of Biointerfaces
Moderator: Joe Baio, Oregon State University


High energy ionizing irradiation produces large amounts of low energy (~20 eV) secondary electrons (SEs). These electrons are produced via a cascade process following the ionization of a core (deeply bound) electron. Due to their low energy there is a high probability for the SEs to become trapped in antibonding orbitals, via resonant scattering, forming a temporary negative ion (TNI) resonance. If the lifetime of the TNI state is long enough, then bond rupture can occur by a process known as dissociative negative ion (TNI) resonance. If the lifetime of the TNI state is long enough, then bond rupture can occur by a process known as dissociative negative ion (TNI) resonance. If the lifetime of the TNI state is long enough, then bond rupture can occur by a process known as dissociative negative ion (TNI) resonance.

The reason for this enhancement could arise from the greater probability of adsorbed tDNA having a significantly higher cross section for radiation damage. Following this approach, we find an unexpected BE shift of a N 1s peak across the series of DNA brushes. Typical effects observed in organic films do not appear to account for the full magnitude of the observed shift, so we will discuss the possible interpretations of this effect and its relation to the structure of DNA brushes.

3:00pm BI+AS-TuA3 Simultaneous 3D Detection of Organics for Intact Samples with Infrared Spectromicrotomography. Carol Hirschmugl, University of Wisconsin Milwaukee

The holy grail of chemical imaging is to provide spatially and temporally resolved information about heterogeneous samples on relevant scales. Synchrotron-based Fourier Transform infrared imaging combines rapid, non-destructive chemical detection with morphology at the micrometer scale, to provide value-added results to standard analytical methods. Hyperspectral cubes of (x,y, z, Abs (λ)) are obtained employing spectromicrotomography2, a label free approach, it inherently evaluates a broad array of wide organic materials, with minimal sample preparation and modification. Examples presented here (polymer composites, single cells and colonies of cells) demonstrate the broad applicability of this approach to detect complex chemical information of intact samples.

Acknowledgements
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4:20pm BI+AS-TuA7 Deep Thoughts: ToF-SIMS Profiling to New Depths. Daniel Graham, L.J. Gamble, University of Washington

The development of aragon cluster sources has opened up new opportunities for ToF-SIMS depth profiling. These sources have enabled depth profiling of a wide range of materials that previously could not be accurately depth profiled. In addition, due to the low damage accumulation and sputtering efficiency of these sources, it is now possible to depth profile through microns of material. This in turn has opened up new opportunities for exploring the 3D chemical environments of a wide range of samples including drug eluting polymers, thick multilayer polymer films and porous tissue scaffolds. However, the ability to dig deeper into samples also results in significant challenges in 3D image reconstruction. For example, due to the fixed geometry of the analysis beam (at 45 deg from the surface normal in our instrument), sputtering away 1 micron of the surface will shift the analysis position by 1 micron. This means that if one were to depth profile 50 microns into a surface, the final image would be shifted by 50 microns. Traditional image registrations methods can be used to accommodate for these shifts, however when digging to depths larger than 10 microns, this requires significantly increasing the initial image size in order to end up with a usable image stack after the image shifting and cropping.

In this presentation we will summarize methods we have been developing to reconstruct deep depth profiles including adjusting the sample height during data acquisition and post acquisition image shifting. We will also show results from a new 3D image overlay tool that enables localization of different chemical environments in 3D and that can show areas of overlap between selected peak area images. These methods and tools will be demonstrated on data from control samples made from polymer beads on silicon and from data taken from polymer tissue scaffolds.

4:40pm BI+AS-TuA8 Development of Novel Pharmaceutical Systems Through Characterisation. David Scour, University of Nottingham, UK

The developments in pharmaceutical delivery systems such as injectable drug eluting microparticles [1], topically applied medicines [2] and wound dressings [3] can be utilised in areas such as the treatment of HIV, basal cell carcinoma and microbial infections respectively. In this study, the characterisation of such systems has been performed using time of flight secondary ion mass spectrometry (ToF-SIMS), x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM).

Injectable controlled release formulations were produced by spray drying two biocompatible polymers, poly(lactic-co-glycolic acid) (PLGA) and polyvinylpyrrolidone (PVP). The samples were analysed using a range of techniques including ToF-SIMS, XPS and AFM showing that the samples were hollow microparticles with a surface PLGA rich phase and an
underlying PVP phase [1]. Additionally, more complex ternary systems incorporating PLGA, PVP and a poorly soluble investigational drug compound were also analysed. These studies also influence the influence of sample processing parameters and drug concentration upon factors such as surface composition which is influential in the drug release properties of the systems.

The permeation of an antibacterial drug, chlorhexidine, into skin tissue has been illustrated using ToF-SIMS chemical imaging of cross-sectioned treated skin samples [2]. This methodology has been further applied to investigate the topical delivery of imiquimod, a drug used in the treatment of basal cell carcinoma. This work demonstrates the ability of the ToF-SIMS technique to correlate chemical species specific to the drug with physiological features within tissue cross-sections. Further application of ToF-SIMS chemical mapping has also been used to successfully differentiate chemically dissimilar regions of anti-microbial films which could be developed as wound dressing materials. Observations made for these materials using combination of ToF-SIMS and AFM analysis revealed the distribution of the active agents upon the surface which would be relevant to the anti-microbial performance.


5:00pm BI+AS-TuA9 Analysis of Peptide Microarrays on Si Using ToF-SIMS. James A. (Tony) Olhuisen, C. James, Sandia National Laboratories, D. Smith, HealthTell, S.A. Johnston, N. Woodbury, Arizona State University

A microarray containing over 1200 each 200µm diameter spots consisting of various length peptide chain monolayers was analysed using Time-of-flight Secondary Ion Mass Spectrometry (ToF-SIMS). This peptide microarray was created using lithographic processes where chains of peptides were built one amino acid at a time. A silane coupling agent was used to attach the peptides to the oxide surface creating a monolayer of peptides directly bonded to the Silicon oxide surface. By tracking ion fragments corresponding to specific amino acids, usually immonium ions, we show that contrast consistent with the number of individual amino acid units in a given peptide dot is generally seen. While some immonium ions are not specific enough to generate clear contrast patterns, most can be used to verify the presence expected amino acids in each peptide dot. Additionally, some amino acids were not found to generate a specific fragment for identification in the positive secondary ion mode.

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5:20pm BI+AS-TuA10 Investigating Tumor Microenvironments with ToF-SIMS. Lara J. Gamble, B. Bluestein, D.J. Graham, University of Washington

Cancer is a heterogeneous malignancy that manifests itself in a variety of morphological types and clinical outcomes. Current evidence indicates that tumor metabolism plays a large role in cancer onset and progression, and its causes and effects are under intense scrutiny. Furthermore, it is of interest to know where changes in tumor metabolism occur within an affected tissue. However, there are few techniques that can specifically interrogate the tumor microenvironment. We use time-of-flight secondary ion mass spectrometry (ToF-SIMS) to determine differences in the chemical composition of the tumor microenvironment of breast cancer tumor tissue samples. Human tissue biopsies from an ongoing trial have been subtyped using DASL genome assay and grouped into subtypes of Luminal B, Basal, and ERRBB2. Images and spectra have been acquired on an IONTOF TOF.SIMS V using Bi+. The ToF-SIMS information, combined with gene expression array analysis, is used to investigate the differences between chemotherapy-resistant tumors and elucidate the underlying mechanisms. Using imaging ToF-SIMS the cellular and stromal regions within the tissue can be separated out as regions of interest (ROI). Imaging principal component analysis (PCA) was successful in separating cellular regions of the tumor and stromal regions when compared with a hemotoxylin and eosin (H&E) stained adjacent tissue slice. Using the ROIs identified from imaging PCA, we compare the chemical differences between cellular and stromal microenvironment chemistry. A comparison of spectral PCA using the entire analysis area vs spectral PCA of ROIs for cellular and stromal regions of the tissue is discussed. The chemistries of these subtypes are compared usingToF-SIMS image and spectral comparison from cellular and stromal regions. A spectral comparison of ROIs between tissue samples using PCA indicates that unique fatty acids distributions may relate to a tumor phenotype and chemotherapeutic resistance.

6:00pm BI+AS-TuA12 Mass Spectrometry using Femtosecond Lasers and Postionization to Characterize Biomaterials Interfaces. Y. Cui, Y.P. Yung, Luke Hanley, University of Illinois at Chicago

Secondary ion mass spectrometry (MS), matrix assisted laser desorption ionization MS, electrospray-based MS and other strategies are widely used for the analysis of intact bacterial biofilms, mammalian tissue, cell cultures, and their interfaces with biomaterials [Bhardwaj & Hanley, Nat. Prod. Rev. (2014) dx.doi.org/10.1039/C3NP0094A ]. The combination of these desorption/ionization methods with high resolution MS and tandem MS capabilities permit metabolomic and proteomic imaging of such samples. Nevertheless, their use to detect many analyte classes within intact biological samples still often suffers from low sensitivity, selective ionization, and/or poor spatial or depth resolution. Laser desorption with ultrashort pulses can remove material from a solid with minimal damage to the remaining sample, potentially allowing both depth profiling and additionally, higher spatial resolution [Cui et al., ACS Appl. Mater. Interf. 5 (2013) 9269]. Furthermore, laser desorbed neutrals can undergo postionization by vacuum ultraviolet or ultrashort pulse radiation for subsequent detection by MS. Postionization has the additional advantage that proper selection of the delay time between the desorption and postionization laser can improve molecular analysis. Here, we demonstrate that proper selection of the delay time between the desorption and postionization by vacuum ultraviolet or ultrashort pulse radiation for the analysis of intact bacterial biofilms, mammalian tissue, cell cultures, and their interfaces with biomaterials is feasible. To achieve such depth profiling, we use laser desorption to remove material from the sample for subsequent analysis. This work demonstrates that ToF-SIMS can be used to study the small molecule imaging capability of these methods on intact, multispecies microbial biofilms and other complex organic/biological samples. Finally, comparisons are made to laser desorption MS under atmospheric pressure.
Environmental Electron Microscopies

Moderator: Jorge Boscoboim, Brookhaven National Laboratory

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

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

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

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

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

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


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

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

References:
1. K. D. Collins and M. W. Washabaugh, Quarterly Reviews of Biophysics, 1985, 18, 323-422.
5:00pm IS+AS+MC+SS-TuA9 Direct Observation of Structure Controlled Carbon Growth by Environmental TEM. J. King, T.W. Hansen, Jakob Wagner, Technical University of Denmark. INVITED
In order to meet the increasing demand of faster and more flexible electronics and optical devices and at the same time decrease the use of the critical metals, carbon based devices are in fast development. Furthermore, the rich resource of carbon element limits the need for recycling and the material supports the friendly environment approach.
Layered carbon structures spanning from graphene to few layered graphite are used for extremely compact devices with outstanding performance [1,2]. A relatively cheap and easy way to produce layered carbon structures on the large scale is via chemical vapor deposition (CVD) growth on catalysts like copper and nickel. However, the exact growth mechanism is still under debate and is most likely dependent on precursor pressure and growth temperature. Here, we have used environmental transmission electron microscopy (ETEM) to follow the growth of layered structures directly at the atomic level and thereby coupling growth rate and quality of the material on the local scale to the growth parameters. Acetylene and methane are exposed to the catalyst (Ni or Cu) in situ in the microscope at pressures ranging from 0.1Pa to 100Pa at temperatures ranging from 500-700C. Following the subsequent appearance of carbon layers allows for determination of instantaneous growth rates under controlled conditions. Single walled carbon nanotube (SWCNT) based electronics is another way of addressing the environment friendly approach of faster and better electronics. In order to exploit the potential of SWCNTs in the electronic industry, controllably, selective growth of either conducting or semiconducting tubes is of high importance. Growing the tubes in the in situ in the ETEM under relevant growth conditions gives fundamental insight in the parameters controlling the chirality and thereby the electronic properties of the SWCNTs.

References:

5:40pm IS+AS+MC+SS-TuA11 In Situ Energy Loss Spectroscopy, A Novel Approach to the Characterization of Surfaces during MBE Growth. Philippe Staib, Staib Instruments, Inc.
A new energy analyzer for Auger Electron Spectroscopy (AES), the Auger Probe, is able to operate in growth vacuum chambers to measure in-situ during growth the composition of the surface [1,2,3]. The primary beam is provided by the RHEED electron gun at a very grazing incidence angle (2 to 3 degrees). The analyzer is also used in EELS mode to measureCharacteristic Energy Losses (CEL). The use of a grazing incidence angle strongly enhances the strength of the energy losses peaks, which become more prominent than the elastic line
EELS data from the Auger Probe are presented showing the evolution of the CEL distributions during oxidation (ZnO), during thermal de-oxidation of GaSb, and during growth of binary and ternary materials (GaAs/GaSb). Surprisingly, even during deposition of homoepitaxial layer, the CEL distributions show a marked dependence upon the flux of material to the sample which can reflect the formation of physical- rather than chemisorbed layers and the smoothness of the surface [4].
The CEL spectra cannot be interpreted simply, due to the strong overlapping of multiple excitations of single energy losses. A model is presented that takes into account the probability distribution for multiple losses, and allows extraction of the el emen tary energy loss lines from the distribution. Using this model, acurate energy loss values can be measured and an effective electron density can be calculated. The intensity of the extracted energy losses versus the intensity of the elastic peak is a measure of the ratio d/ l between the electron path length d and mean inelastic free path l of the specific loss. The inelastic mean free path for each loss line can be deduced using d values from monte-carlo simulation of the electron trajectories and the intensity ratio of the loss peak vs. elastic peak.

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

Nanometer-scale Science and Technology
Room: 304 - Session NS+AS+SS-TuA

Nanowires and Nanotubes: Advances in Growth and Characterization
Moderator: Lincoln Lauhon, Northwestern University

2:20pm NS+AS+SS-TuA1 Surface Chemical Choreography of Nanowire Synthesis. Michael Filler, S.V. Sivaram, N. Shin, I.R. Musin, Georgia Institute of Technology. INVITED
This talk will provide an overview of our recent efforts to understand the chemical phenomena underlying semiconductor nanowire growth. The vapor-liquid-solid technique – where a liquid “catalyst” droplet collects atoms from the vapor and directs crystallization of individual solid layers – is a ubiquitous method for the synthesis of nanoscale building blocks, but a lack of atomic-level design rules prevents robust programming of structure. Long-standing challenges in the control of heterostructure, dopant profile, atomic stacking sequence, kinking, and even simple axial growth restrict the accessible property space and highlight the pitfalls of an overreliance on empirical process optimization. We couple in-situ and ex-situ infrared spectroscopy with post-growth high-resolution electron microscopy to connect specific surface chemical bonds present during synthesis with nanowire structure. Studies of Si and Ge nanowires demonstrate the fundamental, and previously unrecognized, role of adsorbed hydrogen atoms. The surface coverage of these precursor (e.g., SiH4 or GeH4) decomposition intermediates, which we quantitatively determine as a function of pressure and temperature, can change over a narrow range and strongly influence growth. Our findings show, for example, that adsorbed hydrogen is essential for stabilizing the catalyst or driving elongation in new crystal directions for Ge and Si nanowires, respectively. We leverage these insights to rationally design precursors that choreograph nanowire structure on multiple length scales, permitting the fabrication of user-defined defect, kinking, and diameter-modulated superstructures.

3:00pm NS+AS+SS-TuA3 Atom Probe Tomography Analysis of GaAs-AlGaAs Core-Shell Nanowire Heterostructures. Nari Jeon, Northwestern University, S. Morköötter, G. Kohlhammer, Technische Universität München, Germany, L.J. Lauhon, Northwestern University
GaAs-AlGaAs planar heterostructures have various electronic and optoelectronic applications such as solar cells and light-emitting diodes. This is due to a small lattice mismatch between GaAs and AlAs providing wide opportunities in bandgap tuning. Moreover, modulation doping scheme is well-known to be effective in enhancing electron mobility in the heterostructures by minimizing electron scattering from ionized impurities. Since growth of GaAs-AlGaAs core-shell nanowires was demonstrated in 2005, there has been a growing number of papers reporting novel opto-electronic transport properties, which are originated from the nonparallel geometry of GaAs-AlGaAs interfaces and its related
compositional fluctuations. In fact, compositional structures are more complex in the core-shell nanowires compared to the planar counterparts. For example, there are six Al-rich bands along the corners of [110] sidewall facets in the AlGaAs shell. While most of the previous studies were based on transmission electron microscopy on cross-sectional samples, we exploited the atom probe tomography (APT) to explore compositional fluctuations in three dimensions. The focus of the presentation here will be on a study of Si-doped GaAs-AlGaAs core-shell nanowires. Molecular beam epitaxy reactor was used to grow the core-shell nanowires and the GaAs-AlGaAs superlattice planar samples as a reference to the nanowires. Individual nanowires were mounted on tungsten tips using micromanipulator for APT and planar samples were fabricated into tip-shaped APT samples by the lift-out and sharpening method using focused ion beam (FIB). Carefully designed structures of the superlattice with varied thickness and spacing in planar samples enabled us to estimate the range of possible ion beam damage from FIB. The atom probe conditions such as laser pulse energy and target detection rate were also optimized to achieve high spatial and temporal resolutions, which are critical for APT of III-V compound semiconductors where preferential detection loss and surface diffusion for III-V group elements is possible depending on the APT conditions. Intermixing at GaAs-AlGaAs interface and stochiometric fluctuation in AlGaAs shell were mainly studied along with the detection limit of Si dopants in the doping layer.  


III-V semiconductor nanowires (NWs) offer tremendous possibilities for device application in solid-state lightning, energy conversion, and information technology [1]. With their small diameter and their very large surface-to-volume ratio, the NW device combination is strongly determined by their surface structure. Thus, it is both essential and challenging to investigate their atomic surface structure and to combine this information with electrical measurements on individual NWs.  

Recently, we have managed to clean InAs NWs from their native oxide and revealed the atomic arrangement of their side surfaces with scanning tunneling microscopy (STM). Here, we present STM images of various NW surfaces of both wurtzite and zincblende crystal structure [2], including InAs, GaAs, InSb and Nbx WNs. The STM imaging with scanning tunneling spectroscopy (STS) measurements, we simultaneously study the surface structure and local electronic properties across the interfaces of NW heterostructures [3].  

For correlating local structural and electronic characterization with transport measurements of NW devices, we have developed a novel STM-based setup: We are using combined atomic force microscopy (AFM) and STM/AFM on individually contacted NWs for mapping the surface structure and the local band alignment along the NW heterostructure under device performance. We show initial results of this unique approach on InAs-GaSb nanowire tunnel diodes, where we could prove Esaki behavior of a NW while it was investigated by STM/AFM. From a set of STS spectra we determined the position of the Fermi level along the nanowire for different applied biases, showing an abrupt drop directly at the material interface. In a reverse experiment, we used the STM/AFM tip as local gate and measured the resulting source-drain current through the nanowire for different biases [4].  

In some cases it is desirable to measure the conductivity of individual as-grown nanowires in an upright-standing configuration without any sample processing. Here we have developed an alternative setup where the STM tip is used to first image free-standing nanowires from top and then form a point contact [5]. We will demonstrate the reproducibility of this method in establishing the low-energy interband conductance of individual InP and InAs nanowires [6], and we will show initial results on the I-V properties of individual InP NW solar cells.  

Thin Film
Room: 305 - Session TF+AS+EM-TuA

Thin Film: Growth and Characterization II
Moderator: Mark Davidson, University of Florida

2:20pm TF+AS+EM-TuA1 A Statistical Optimization of Perpendicular Anisotropy and Damping for Ta-Inserted Double CoFeB/MgO Interface MTJ's, S. Gupta, Samuel Schwarz, B. Clark, University of Alabama

A statistical Design of Experiments was conducted on double-interface Ta-inserted CoFeB/MgO magnetic tunnel junctions (MTJ's). These MTJ's were deposited using a Shamrock planetary sputtering system. The thicknesses of the inserted Ta and the CoFeB electrodes were varied using Response Surface Methodology. The responses measured using magnetometry and ferromagnetic resonance were a) effective magnetization, b) damping constant and c) perpendicular anisotropy. The effect of annealing on the perpendicular anisotropy was also observed for these devices. As the Ta thickness is increased for fixed CoFeB thickness, the M-H loops indicate that the anisotropy is becoming perpendicular. After annealing, both magnetometry and FMR results show that the MTJ's indicate full perpendicular anisotropy. Interfacial perpendicular anisotropy, which can be extracted from the FMR measurements, scales with the...
The thin films can be described as a mixture of silicon and titanium oxide at the atomic scale rather than two separate SiO2 and TiO2 phases. These mixed oxide layers are basically amorphous and exhibit good morphological properties provided the titanium content is lower than the silicon one.

On the whole these TiSiO layers offer a good compromise in terms of morphological, optical and electrical properties.

4:20pm TF+AS+EM-TuA7 Kinetically-Limited Lattice Relaxation in Linearly- and Non-Linearly- Compositionally-Graded InGaAs/GaAs (001) Metamorphic Heterostructures, Tadei Kujiñfsa, J.E. Ayers, University of Connecticut

Metamorphic buffer layers allow tremendous flexibility to design novel InGaAs/GaAs semiconductor heterostructures for application in various microelectronic and optical devices. However, device fabrication, reliability and performance are limited by dislocation defects associated with the growth of highly mismatched systems such as InGaAs on GaAs substrate. Thus, understanding kinetically-limited lattice relaxation and development of a plastic flow model applicable to multilayered and compositionally graded heterostructure is desirable to provide guidance in designing InGaAs/GaAs devices. Previously, we reported a plastic flow model for rather large, efforts are also devoted to NbTiN which has similar structures. We note though that since the intrinsic resistivity of NbN is lower critical field, Hc1, and the residual resistance ratio. Beringer

5:40pm TF+AS+EM-TuA9 Superconducting Properties of NbN and NbTiN Thin Films, Matthew Burton, M.R. Beebe, R.A. Lukaszew, D. Beringer, College of William and Mary

Thin films of NbN and NbTiN are promising materials currently researched for improvements in superconducting radio frequency (SRF) technology and applications. At present, bulk niobium SRF accelerating cavities suffer from a fundamental upper limit in maximally sustained accelerating gradients; however, a scheme involving multi-layered superstructures consisting of superconducting-insulating-superconducting (SIS) layers has been proposed to overcome this fundamental material limit of 50 MV/m [1]. The SIS multi-layer paradigm is reliant upon implementing a thin shielding material with a suitably high Hc1 which may prevent early field penetration in a bulk material layer and consequently delay the high field breakdown. It has been predicted that for thin superconducting films — thickness less than the London penetration depth (~200 nm in the case of NbN) — the lower critical field Hc1 will be enhanced with decreasing thickness. Thus, NbN thin films with a high Hc1 value are possible candidates for such SIS structures. We note that though since the intrinsic resistivity of NbN is rather large, efforts are also devoted to NbTiN which has similar superconducting properties but much lower intrinsic resistivity which is significant.

5:00pm TF+AS+EM-TuA12 Structural, Electrical, and Optical Characterization of Impurity-Dependent, Ultra-Low-Dislocation-Density Ge Epitaxially Grown on Si and Characterization of MOSFETs Fabricated on Ge-on-Si, Swapnadip Ghosh, S.M. Han, University of New Mexico

Building on a simple two-step MBE growth technique, we have investigated possible dislocation locking mechanisms by dopant impurities, coupled with artificially introduced oxygen (O). In the case of n-type Ge grown on Si, our materials characterization indicates that the dislocation density (DD) can reach the ~10^12 cm^-2 level, compared to p-type and undoped Ge on Si (GeO). We note that our Ge film covers the entire underlying Si substrate at the wafer scale without mesas or limited-area growth. In this presentation, we will focus on the use of n-type impurity (phosphorus) diffusion from the Si substrate and the introduction of O at the Ge-Si interface. The O is introduced by growing a thin chemical SiO2 layer on top of the Si substrate before Ge epitaxy begins. Z-contrast cross-sectional TEM images suggest the presence of O precipitates in n-type Ge, whereas these precipitates appear absent in p-type Ge. These O precipitates are known to lock the dislocations. Supporting the argument of precipitate formation, the TEM shows Moiré fringes due to various phase boundaries that exist at the precipitate/Ge-crystal interface. We speculate that the formation of phosphorus (P) segregation resulting from slow diffusion of P through precipitates at the precipitate/Ge-crystal interface facilitates dislocation locking. Impurity segregation in turn suppresses O concentration in n-type Ge leading to the reduced DD that appears on the top surface of n-Ge compared to p-Ge film. The O concentrations (10^11 to 10^13 cm^-2) in the n- and p-type Ge films are measured using secondary ionization mass spectroscopy. We have then compared the structural and electrical characteristics of n-type Ge films with its p-type counterparts. In n-type Ge, the DD decreases from ~10^12 cm^-2 near the Ge-Si interface to ~10^10 cm^-2 at the film surface. In contrast, we observe 5x10^10 cm^-2 DD at the film surface in p-type Ge. The full width at half-maximum for our n-type Ge (004) XRD peak is 100 arcsec, compared to 230 arcsec of p-type Ge. As a stringent test of the dislocation reduction, we have also fabricated and characterized high-mobility MOSFETs on Ge substrates. We also report p- and n-MOSFETs with μ_eff of 401 and 940 cm^2 V^-1 s^-1 and a subthreshold slope of 100 and 200 mV/decade, respectively. These effective mobilities show an exceptional 82 and 30% improvement over that of conventional Si channel MOSFETs. We also investigate the optical quality of ultra-low DD Ge film by measuring photoluminescence (PL). Then-type Ge PL main peak shows pronounced tensile-stain (~0.8%) than that of p-type, which is an indicator of Ge,Sn alloying the Ge band-edge.
Chemical Imaging in 2D and 3D

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

Secondary ion mass spectrometry (SIMS) has been increasingly utilized for single cell imaging owing to its unique combination of spatial resolution and chemical differentiation by mass. Depending on the instrument type, subcellular lateral resolution between 50’s and 100’s of nanometers can be obtained, sometimes with both elemental and organic information obtained simultaneously, and sometimes with highly precise isotopic ratio measurements being attainable. However, imaging at the limits of the technique requires sufficient counts per pixel, which can be limited by analyze concentrations, competitive ionization pathways, and cumulative cluster ion beam damage accumulation. This work focuses on the advantages and disadvantages of combining focused ion beam (FIB) milling of single cells with subsequent ToF-SIMS imaging, as well as using large geometry (LG)-SIMS for high mass resolution analysis of single cell components that would otherwise not be easily detectable in other instrumental configurations. Such developments expand the research areas that are possible for single cell SIMS analyses, including cell differentiation without relying on multivariate analyses and targeted cell uptake studies.

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

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

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

The long term aim of developing these protocols is to be able to acquire high resolution chemical images of single biological cells. So far, it appears that differential sputtering effects are not too serious for these samples. The combined SIMS/AFM strategy developed here will be important for verifying these initial observations. Finally, there is an emerging interest in gas cluster ion sources, namely A_{m}X_{n+2m}, since even lower chemical damage than C_{60} is observed, and the depth resolution during erosion appears to be less than 5 nm. Here we show that the combination of C_{60} imaging and A_{m}X_{n+2m} sputtering provides an even more powerful protocol. In general, we show that the AFM/SIMS combination is a powerful tool for 3-dimensional chemical imaging.
residual down to the few micron level, this greatly enhances the capability of XPS instrumentation to image novel carbon surfaces and devices.


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

INVITED

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

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

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

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


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

Biomaterial Interfaces

Room: 317 - Session BI+AS+WeM

Nonlinear Optical & Vibrational Spectroscopy

Moderator: Luke Hanley, University of Illinois at Chicago

8:40am BI+AS+WeM3 Characterizing Adsorbate Structure at the Solid-Liquid Interface through Nonlinear Vibrationa Spectroscopy and Modelling Approaches. S. Roy, P.A. Covern, K.-K. Hung, U. Siege, Department of Physics, University of Victoria, Canada

INVITED

Even-order nonlinear spectroscopies such as second harmonic (SHG) and sum frequency generation (SFG) are valued for their sensitivity to interfacial structure since they are capable of discriminating from adjacent bulk phases based on symmetry. Visible-infrared SFG spectroscopy additionally harnesses the sub-molecular structural probe of a vibrational spectroscopy by tuning the infrared laser over molecular resonances. As a result, over the past two decades, SFG spectroscopy has been successfully applied to a wide variety of solid, liquid, and vapor interfaces, revealing signatures of the molecular organization that provide clues to the surface structure. Our group has been working on techniques to assist in the molecular interpretation of the SFG response. For small molecules, this includes grid computing-based searches to validate candidate orientation distributions based on the experimental data. For larger molecules with additional conformational flexibility, we employ molecular dynamics simulations to further refine our efforts to interpret the SFG data. Our most recent efforts explore the use of phase-resolved SFG spectra in order to develop more sensitive functions for scoring trial molecular orientation distributions. Our goal is to develop tools that are scalable to molecules of arbitrary complexity. This talk will provide some examples to illustrate our path towards this direction.

9:20am BI+AS+WeM5 Vibrational Spectroscopy Investigation of the Giant Surface Potential of Organic Semiconductors. Laura Kraya, Princeton University, C. Krekeler, C. Weigel, Technical University Braunschweig, Germany, P. Zhao, Princeton University, W. Kowalski, Technical University Braunschweig, Germany, C. Lennartz, BASF, A.L. Kahn, B. Koel, Princeton University

A phenomenon known as the giant surface potential (GSP), where the surface potential of organic films display linear growth with increasing film thickness in the absence of light was first reported by Ito et al. on (8 hydroxyquinoline)aluminum(Alq3), a prototypical fluorescent material used in OLEDs. It has been shown that the surface potential of Alq3 has reached 28 V for a 560 nm thick film by Kelvin probe measurements in vacuum in the absence of light. Since then this phenomenon has been observed for a broad range of molecules thermally evaporated on varying substrates under similar conditions. The effect is independent of the substrate, dependent on film thickness and decays quickly with illumination at the normal mode of the respective molecule. The spontaneous buildup of the GSP cannot be explained by any classical interfacial phenomena. Investigations into the cause of GSP, including the analysis of light and heat on the surface potential, are not yet understood.

In this study we use vibrational spectroscopy to understand the nature of the GSP buildup, where we have found a significant change in the vibrational structure of the organic material in thick films where the GSP is present as compared to thin films. The vibrational spectra of the most commonly studied light-emitting material, Alq3, on indium tin oxide (ITO) is investigated as a function of thickness using high resolution energy electron loss spectroscopy (HREELS), Ramsan spectroscopy, high resolution x-ray photoelectron spectroscopy (XPS), and Modelling Approaches. For optical remote sensing, a wide variety of solid, liquid, and vapor interfaces, revealing signatures of the molecular organization that provide clues to the surface structure. Our group has been working on techniques to assist in the molecular interpretation of the SFG response. For small molecules, this includes grid computing-based searches to validate candidate orientation distributions based on the experimental data. For larger molecules with additional conformational flexibility, we employ molecular dynamics simulations to further refine our efforts to interpret the SFG data. Our most recent efforts explore the use of phase-resolved SFG spectra in order to develop more sensitive functions for scoring trial molecular orientation distributions. Our goal is to develop tools that are scalable to molecules of arbitrary complexity. This talk will provide some examples to illustrate our path towards this direction.

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a different molecular orientation exists at the interface than in the bulk, where the GSP exists.

9:40am BI+AS-WeM6 Diatom Biomineralization at the Molecular Level Probed by SFG Spectroscopy, H. Lutz, Max-Planck-Institute for Polymer Research, Germany, J.E. Baio, Oregon State University, V. Jaeger, A. Roehrig, G. Drobny, J. Pfleauder, University of Washington, Tobias Weidner, Max-Planck-Institute for Polymer Research, Germany
Specialized mineral proteins control the growth of biogenic hard tissue. Using specific recognition motifs, proteins bind and release mineral facets and grow the intricate mineral morphologies found in Nature. Particularly fascinating examples of biomineralization are the high fidelity silica nanostructures in the shells of diatoms. Within the unicellular algae Cylindrotheca fusiformis, proteins called silaffin play a crucial role in the molecular biomineralization machinery. In order to harness the concepts used by Nature to efficiently fabricate mineral nanostructures we aim to understand the underlying protein-silica interactions. We found that artificial peptides consisting of lysine and leucine (LK peptides) can mimic silaffin’s capability of forming various biosilica nanostructures. These peptides were designed to adopt helical or beta-sheet structures due to their hydrophobic periodicities and represent simple model systems to study the effect of protein folding on mineralization. Using surface sensitive sum frequency generation (SFG) vibrational spectroscopy we have studied the interactions of LK peptides with biosilica surfaces and within biosilica composites. We monitored how different LK peptides fold at the silica-water interface and we found that interfacial folding is crucial for the silica morphology: spheres, rods and flakes were produced by LKs – depending on their surface folding. Side chains also actively participate in the mineralization process. We probed the side chain structure of LKs in contact with silicic acid solution and observed increased ordering of charged lysine side chains during the formation of biosilica, indicating their involvement in silica nucleation. Combined with cryo-TEM measurements and MD simulations of different stages of nanoparticle nucleation the SFG studies provide important details of peptide-driven silica formation.

11:00am BI+AS-WeM10 Water, Charge and Membrane Interface Stability, Sylvie Roke, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
Life occurs in three dimensional turbid aqueous systems. A cell consists for ~60 % of water and contains many organelles and interfaces. The average distance between two molecules, or a molecule and a membrane interface is approximately 1 nm. The molecular, structural, dynamic, and biological properties of water, aqueous systems and aqueous interfaces are essential in understanding the complexity of life, and our ability to harness its features for novel (nano)technologies.
Here, I will introduce nonlinear light scattering methods that can be used to gain label-free molecular level information about model membrane interfaces in liquid aqueous nanoscopic systems. The use of these methods will be illustrated around the following questions:
· Does water behave charge asymmetrically?
· What is the role of water in determining the stability of amphiphilic interfaces?
· Is the molecular structure of model membranes influenced by the above considerations?

11:40am BI+AS-WeM12 Second Harmonic Scattering: Characterizing the Interaction between Lipid Membranes and Water, Cornelis Lütgebeckus, C. Macias-Romero, S. Roke, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
Lipid membranes are essential for all organisms by separating functional compartments and mediating cellular signaling. Dioleoylphosphatidyloleholine (DOPC) and Dioleoylphosphatidylethanolamine (DOPS) are the main constituents of mammalian cell membranes. Molecular level understanding of cell membrane architecture often involves supported lipid membranes and invasive methods. We designed a second harmonic scattering (SHS) instrument that allows for investigating the molecular properties of interfaces from lipid vesicles in aqueous environments, label-free, and substrate independent. Characterizing DOPC:DOPS composited liposomes, we find that the water-lipid interaction is mainly responsible for the SHS signal. Moreover, the SHS signal increases up to a lipid mixing ratio of 9:1 and remains unchanged at lower ratios. This value coincides with the saturation value of DOPS in the outer leaflet of the mammalian membrane, when spontaneous apoptosis occurs.

12:00pm BI+AS-WeM13 Analyzing the Structure of Amyloid Fibrils in Bacterial Biofilms In Situ and in Real Time Using Sum-Frequency-Generation Spectroscopy, P. Johansson, B. Francisco, J. Bryer, Patrick Koelsch, University of Washington
Curli fimbriae are thin, needle-like structures formed by proteins. These so-called amyloid fibrils are typically associated with neurodegenerative conditions such as Alzheimer and Parkinson’s disease; however, they can also play a beneficial role in various other processes in nature. Curli fimbriae have been shown to be involved in e.g. the colonization of abiotic surfaces, biofilm formation, and internalization of bacteria into eukaryotic cells. The structure of amyloid fibrils has been studied by IR spectroscopy, far UV CD spectroscopy, NMR, scanning probe techniques, and fluorescent probes that bind to fibrils. What is common to those approaches is the need for labelling or an ex vivo character, typically involving purification steps. Here we show how to use sum-frequency-generation (SFG) spectroscopy to study the structural stages of amyloid fibrillation within biofilms formed by a Pseudomonas strain of the P. fluorescens group. Studies have been performed in vitro, over several days of biofilm formation, under defined environmental conditions, and in real time - without the need for labels or any other disruptive sample preparation. In addition to the wild-type strain, genetically modified P. fluorescences were studied that are either overexpressing fibrils, or for which the fibrillar formation was suppressed. Furthermore, SFG spectra from purified amyloids were used to correlate in vitro and ex vitro results.

Energy Frontiers Focus Topic
Room: 315 - Session EN+AS+EM+SE-WeM
Thin Film Photovoltaics
Moderator: Rachel Morrish, Colorado School of Mines
8:20am EN+AS+EM+SE-WeM2 Epitaxy and Nanochemistry of CdS on CuIn,Ga)Se2 for Photovoltaic Devices, X. He, University of Illinois at Urbana Champaign, H. Tellez, J. Druce, Kyushu University, Japan, K. Demirkan, Miasole, P. Ercius, Lawrence Berkeley National Laboratory, V. Lordi, Lawrence Livermore National Laboratory, J. Kilner, Imperial College London, UK, T. Ishihara, Kyushu University, Japan, Anglo Rocker, University of Illinois at Urbana Champaign
CuIn,Ga)Se2 (CIGS) photovoltaics are very promising candidates for high-performance energy generation from sunlight. They typically include a heterojunction between CdS and CIGS. The nature of that heterojunction is critical to the performance of the devices. We present experimental results on the nanochemistry of CIGS and CIGS/CdS heterojunctions and the nanostructure of the junctions. In particular we present low energy ion scattering (LEIS) results on epitaxial single crystal CIGS and CIGS/CdS heterojunctions formed by chemical bath deposition of CdS. Also shown are results of high-resolution transmission electron microscopy (TEM) studies of the CIGS/CdS heterojunction where the junction is formed by physical vapor deposition. LEIS has single-atomic-layer chemical sensitivity that provides a unique ability to distinguish the nanochemical nature of CIGS surfaces and heterojunctions. TEM provides both nanostructural information and the possibility to determine the chemistry of the junction on the nanoscale by energy dispersive spectroscopy and energy filtered imaging. Complete epitaxy of the CdS throughout its ~50 nm thickness is observed in the physical-vapor-deposited CdS. Domains of cubic zincblende and hexagonal wurzite structure CdS have been observed. Twins in the CIGS grains were found to propagate into and often through the CdS layer, resulting in a twin or grain boundary in the CdS. The CdS epitaxial relationship and the effect of surface steps on the CIGS surface are shown. The nanochemical analysis results show significant penetration of Cu into the CdS layer, although no alteration in the CdS nanostructure is observed. The other elements show an abrupt nanochemical junction. LEIS results show the presence of segregated layers on the CIGS surface and further refine the nature of the nanochemical intermixing across the interface.

8:40am EN+AS+EM+SE-WeM3 Microstructure Development in Colloidal Nanocrystal Coatings, B.D. Chernomordik, M. Ketkar, K. Hunter, A.E. Béland, Eray Aydil, University of Minnesota
A potentially high-throughput and inexpensive method for making CuZnSn(Sx,Se1_x) (CZTSx) thin film absorber layers for solar cells is annealing colloidal nanocrystal coatings cast from colloidal dispersions of CTS and Zn nanocrystals (NCs). The nanocrystal coatings can be annealed in sulfur or selenium atmosphere to make CZTS or CZTSx, respectively. During annealing, the nanocrystal films can transform into polycrystalline thin films with micrometer-size grains. Understanding the roles of key annealing
parameters in the development of microstructure in CZTSSe thin films is critical for achieving inexpensive and high-efficiency CZTSSe solar cells. In this presentation, we will discuss the effects of contaminants such as selenium vapor pressure, annealing temperature, substrate, and e eating ramp-rate on the microstructure development in CZTSSe films and contrast the results with films annealed in sulfur. By using a closed system, rather than a flow furnace, we can quantify and systematically control selenium pressure. Annealing films at high selenium pressure (450 Torr) leads to the formation of a sulfuric-25-S-grown top of a nanocrystalline layer that is rich in carbon. This segregation of carbon at the CZTSSe-substrate interface is commonly ascribed to the formation of a capping/blocking layer of CZTSSe grains, which trap the carbon, originating from the ligands on NC surfaces, beneath these grains. However, we found that a continuous layer of CZTSSe grains is not necessary to observe carbon segregation into the film-substrate interface. In contrast, films annealed with sulfur do not show such distinct carbon-rich layers and most of the carbon volatilizes from the film during annealing. Increasing the heating ramp-rate to the annealing temperature eliminates the formation of carbon-rich layers and results in grains that are approximately 500 nm. We will discuss the results of a series of experiments which led us to conclude that Se condensation during annealing may play a key role in grain growth and carbon segregation.

9:00am EN+AS+EM+SE-WeM4 Effect of Chemical Wet Cleaning on Surface Composition and Work Function of Thin Film CZTSSe, Kasra Sardashti, University of California at San Diego, E.A. Chagarov, T. Kaufman-Osborn, University of California, San Diego, S.W. Park, University of California San Diego, R. Haight, W. Wang, D.B. Mitzi, IBM T.J. Watson Research Center, A.C. Kummel, University of California at San Diego Polycrystalline Copper-tin-zinc-sulfide/Se (CZTS,Se) compounds have received wide research interest due to their potential as inexpensive absorber materials composed earth-abundant elements. Photovoltaic devices fabricated on CZTSSe has reached the highest (or record) conversion efficiency of the 12.6%. One of the key parameters to further boost the conversion efficiency is to control the concentration of combination sites at the surface, in the grain boundaries, and in the bulk. Surface states formed on the sample surface as a result of carbon and oxygen contamination can act as non-radiative recombination sites which limit the ultimate cell efficiency. Therefore, a surface-cleaning method which can effectively reduce the amount of surface oxygen and carbon is necessary for CZTSSe processing. In this work, two mm thick CZTSSe films were prepared by spin coating hydrazine-based precursor solutions onto Mo-coated soda lime glass substrates in a nitrogen-filled glove box. To clean the CZTSSe surfaces, three different wet cleaning recipes were used: a) NH4OH only; b) HCl followed by NH4OH; 3) H2O2 followed by NH4OH. The effect of the wet cleaning on the surface composition including carbon and oxygen content has been studied via X-ray photoelectron spectroscopy (XPS) and femtosecond ultraviolet photoelectron spectroscopy (fs-UPS). Spatial variation of work function over the surface upon surface cleaning was measured via Kelvin Probe Force Microscopy (KPFM). The stability of the clean surface against reoxidation in ambient was modeled by density functional theory (DFT). The H2O2/NH4OH recipe showed the best result reducing the amount of surface O and C down to 5% and 20%, respectively. This is due to the oxidizing effect of H2O2 which converted the carboxaceous surfaces contaminants into oxides which were later removed by NH4OH. DFT calculations are consistent with a group VI surface being stable against oxidation by ambient moisture. KPFM measurements showed strongly non-homogeneous surfaces after both NH4OH-only and H2O2/NH4OH clean. Areas with work function different from CZTSSe could be the binary chalcogenides formed during the growth and were covered by a native oxide. NH4OH etch successfully removed these native oxides made those phases visible to KPFM.

9:20am EN+AS+EM+SE-WeM5 Phase Transformation, Surface States, and Electronic Structures of Pyrite Thin Films Under In Situ Heating and Oxygen Gas Exposure, Yu Liu, N. Berry, Y.N. Zhang, University of California Irvine, C.C. Chen, Argonne National Laboratory, H. Bong, Z. Liu, Lawrence Berkeley National Laboratory, R.Q. Wu, M. Law, J.C. Hemminger, University of California Irvine Iron pyrite (cubic FeS2) with its exceptional optical absorption and suitable band gap is promising a earth-abundant semiconductor for thin film solar cells. Using ambient pressure synchrotron x-ray spectroscopies, we report the nanoscale depth profiles of surface and electronic structures for phase-pure pyrite thin films under in situ heating and oxygen gas exposure. Polaronic x-ray absorption spectra show that absorption on the L-edge shifts closer to the Fermi surface with increasing temperature. The XAS line shapes of Fe and S L-edge provide the information of ligand crystal field environment and the phases of the FeS2 particles. We also report the non-destructive photoemission depth distributions of sulfur defects, vacancies, impurities and oxide as a function of temperature and oxygen dose. Valence band spectra indicate a band gap narrowing related to the temperature and phase transition from pyrite (FeS2) to pyrrhotite (Fe1-xS) occurs above 430 °C. In addition, our results under in situ oxygen gas exposure suggest that the surface mono sulfide species is oxidized first, and the reduction in the total density of states near the Fermi surface is caused by oxide layers of sulfate like and iron oxide products on the top ~2 nm.

9:40am EN+AS+EM+SE-WeM6 Improvement of SnS-based Photovoltaic Devices via Reverse Engineering of the Voc and Study of Optimal n-Type Material, Rona Banai, N.J. Tanen, J.J. Cordell, J.R. Nasr, R.E. Urena, H. Lee, J.R.S. Brownson, M.W. Horn, Penn State University Tin (II) Monosulfide (SnS) has theoretical promise as a new material for thin film photovoltaics (PV). Despite a full decade of rigorous research to develop high-performance devices, improvement beyond single-digit percent efficiencies seems unattainable. Engineering this material into a usable device is crucial for future development. Our group has been investigating the optical and structural properties of magnetron sputtered SnS, thin films [1,2,3]. This work will investigate the properties that govern open-circuit voltage, including band gap, series resistance, carrier concentration and built-in potential. Some of these parameters are directly related to the junction material paired with SnS. Several partner materials will be presented with p-SnS including, but not limited to highly doped n-ZnO and n-SnS. Current work is underway to produce n-type SnS as well which would have potential to produce a homojunction. The optoelectronic properties of SnS make it a suitable material for PV. Its high absorption coefficient, greater than 105 cm−1, and band gap near 1.3 eV are well matched with the solar spectrum. SnS also has a carrier concentration greater than 1018 cm−3 and potential to be both n-type and p-type. Our group is able to produce dense SnS thin films with optimal electronic properties. Sputtering the material gives great control over the material properties and recent work optimizing post-deposition heat treatment has shown great promise for improving the material.

Tin sulfide thin films were sputtered on glass and oxidized silicon substrates at varying substrate-to-target distances, substrate temperature, target power, and chamber pressure. The sputter target was a 3” SnS2 with 99.999% purity (LTS Research Laboratories, Inc.). These sulfur-rich samples were then dipped under medium concentration (2×10−3 M) in the deposition chamber at 400°C to produce a uniform a-SnS, which is most likely to be p-type. Producing n-type SnS is possible via annealing of the films in a methanol/SnCl4 solution. Production of homojunction SnS-based thin film devices is not found in the literature. Our work aims to produce these devices for the first time and compare them to a well-known partner material such as ZnO.

In recent years Zn-IV-N$_2$ compounds have seen increased interest as New Zealand Kennedy, Effects on the Fundamental Bandgap of ZnSnN$_2$ onsets occur at higher energy in films with lower carrier concentrations. As state lighting applications. Several reports of successful growth for the Ge price fluctuations due to limited domestic supply, lack of recycling and on the Sn containing member of the family. This material offers a possible 3-10x10$^{21}$ cm$^{-3}$ range for which we would expect a significant Burstein-Moss Shift, but in a manner consistent with a variation in the disorder for this material; this narrowing behavior is consistent with observed variations in absorption spectra. Of practical interest is the disorder for this material; this narrowing behavior is consistent with a variation in the disorder for this material; this narrowing behavior is consistent with observed variations in absorption spectra. Of practical interest is the possibility of a material with a tunable bandgap without the need for traditional alloying. Zn-Sn-N$_2$ is expected to have a bandgap varying from 1.1 to 2 eV controlled by the continuous degree of order in the cation sublattice. Although hard X-ray diffraction measurements of these films do not show a variation from a hexagonal structure, Hall measurements of carrier concentrations compared with absorption data indicates that our samples vary their absorption onset, not as would be expected from Burstein-Moss Shift, but in a manner consistent with a variation in the lattice order. DFT calculations indicate that there is a variation in the Density of States between the ordered and disordered films. Films which were consistent with increased order absorption are also consistent with an increased order density of states measured by HAXPES.

This project is supported by NSF grant DMR1244887 (Program Director Charles Ying), and EPSRC grant EP/G004447/2.

11:40am EN+AS+EM+SE-WeM12 Inhomogeneity of p-n Junction and Grain Structure of Thin Film CdTe Solar Cells Studied by Electron Beams, Haeyoun Yoon, P. Haney, NIST, P. Koirala, University of Toledo, J.J. Basham, Y. Yoon, NIST, R.W. Collins, University of Toledo, N. Binghamton University, NIST

Thin film CdTe solar cells are a promising photovoltaic (PV) technology in today’s market due to their high optical absorption and insensitive fabrication processes. However, the current module efficiency is well below the theoretically estimated maximum efficiency (13 % vs. 30 %). Recent studies have suggested that inhomogeneity of the PV materials is mainly responsible for the low power conversion efficiency. In this work, we investigate the variation of local PV properties of CdTe solar cells, focusing on grain boundary properties. TiO$_2$-CdTe solar cells doped 5x10$^{18}$ cm$^{-3}$ p-type CdTe were sputtered on a TCO (transparent conductive oxide) coated glass substrate followed by CdCl$_2$ treatment. The back contact metals (3 nm Cu / 30 nm Au) were deposited and annealed, creating 256 devices in a 15 cm by 15 cm solar panel. Following light and dark current-voltage measurements, we performed local characterizations using electron beams for high (> 13 %) and low efficiency (< 6 %) devices within the panel. Electron beam induced current (EBIC) was used to measure the local carrier collection efficiency with a spatial resolution of ~20 nm excitation carriers either from the top surface or the cross-sections of the devices. Cross-sectional EBIC data reveals that the peak of efficiency is in the middle of CdTe layer in the low efficiency devices, while the carrier collection is maximal near the p-n junction in the high efficiency devices. The EBIC contrasts at grains/grain boundaries in these devices are also compared. The measured local electronic properties are correlated to microstructural morphology (Transmission Electron Microscopy), orientation (Electron Back Scattered Diffraction), and chemical composition (Energy Dispersive X-ray spectroscopy). We perform 2D model drift-diffusion simulations to determine the magnitude of downward band-bending near grain boundaries (with typical magnitude of 0.2 eV). We will discuss the impact of carrier generation rate (high level injection vs. low level injection) in EBIC analysis.

12:00pm EN+AS+EM+SE-WeM13 Micro-Structural Activation Mechanisms in Thin Film CdTe Photovoltaic Devices, John Walls, A. Abbas, J.W. Bowers, P.M. Kaminski, Loughborough University, UK, K. Barth, W. Samath, Colorado State University

Thin Film CdTe photovoltaics is a commercially successful second generation technology now used extensively in solar energy generation at the utility scale. Although the cadmium chloride treatment is a process that is essential to produce high efficiency devices, the precise mechanisms involved in the re-crystallization and associated improvement in electronic properties have not been fully understood. In this paper we report on the application of advanced micro-structural characterization techniques to study the effect of the cadmium chloride treatment on the physical properties of the cadmium telluride solar cell deposited by both close space sublimation (CSS) and magnetron sputtering and relate these observations to device performance. In particular, High Resolution Transmission Electron Microscopy (HRTEM) reveals that the untreated material contains high densities of planar defects which are predominantly stacking faults and that the optimized cadmium chloride treatment removes these completely with only twins remaining. Parallel theoretical studies using Density Functional Theory (DFT) shows that certain types of stacking fault are responsible for the poor performance of the untreated material. Extending the treatment time or increasing the annealing temperature above ~400°C improves the microstructure but results in lower efficiency devices. Composition–depth profiling using XPS and SIMS reveals that this deterioration in performance is linked with chlorine build up at the CdS/CdTe junction. These experiments and parallel theoretical studies have improved our understanding of the mechanisms at work in the cadmium chloride assisted re-crystallization of CdTe and could lead to further increases in device efficiency.

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

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

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

In this talk, it will be shown a series of in-situ techniques [X-ray diffraction (XRD), pair-distribution-function analysis (PDF), X-ray absorption spectroscopy (XAS), environmental scanning tunneling microscopy (ESTM), infrared spectroscopy (IR), ambient-pressure X-ray photoelectron spectroscopy (AXPS)] can be combined to perform detailed studies of the structural, electronic and chemical properties of metal/oxygen catalysts used for the production of hydrogen through the water-gas shift reaction (WGS, CO + H$_2$O → H$_2$ + CO$_2$). Under reaction conditions most WGS catalysts undergo chemical transformations that drastically modify their composition and properties during the synthesis process. The active phase of catalysts which combine Cu, Au or Pt with oxides such as ZnO, CeO$_2$, TiO$_2$, CeO$_2$/TiO$_2$ and Fe$_2$O$_3$ essentially involves nanoparticles of the reduced noble metals. The oxide support undergoes partial reduction and is not a simple spectator, facilitating the dissociation of water and in some cases modifying the chemical properties of the supported metal. Therefore, to optimize the performance of these catalysts one must take into consideration the properties of the metal and oxide phases. IR and AP-AXPS have been used to study the reaction mechanism for the WGS on the metal/oxyde catalysts. Data of IR

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Reactions with 9:20am structure of the FeIL will be discussed. Measurements at various states of charge, and the structure of the molecule absorption fine structure (XAFS) spectroscopy. We conduct our

The surfaces of heterogeneous catalysts in reactive environments are dynamic and require

adjacent Fe atoms, resulting in antiferromagnetic coupling between the
to the metal center occurs primarily through the alcohol groups. Cyclic

to the paramagnetic Fe center. It is believed the coordination of the ligand

traditional methods such as NMR to probe surface chemistry are limited due

5-6M, and improves the energy density of the system. However, little is

the discharged product is retained on the vehicle, and can be subsequently

eunique gases which are the charged

energy into the battery, discharged, and then removed to storage containers. This makes the

battery, which uses liquids that are pumped into the battery to be charged or

contenders for a battery that can quickly be recharged is a redox flow

Energy storage for vehicles is advancing rapidly, and one of the possible

in situ characterization of Metal-

Based Ionic Liquids using X-ray Spectroscopy, Robert Meulenber

University of Maine, C. Apblett, H. Pratt, T. Anderson, Sandia National Laboratories

Energy storage for vehicles is advancing rapidly, and one of the possible

To date, however, the concentrations of most redox flow battery chemistries have been low, below the 1-2M concentration level. Recently, a new type of ionic liquid (IL) redox flow battery chemistry has been developed that involves ionic liquids based on 1-ethyl-3-methylimidazolium (EMI) cations and tetraethylammonium (TEA) anions with a 1:1 e+/e- stoichiometry. These ILs are liquid at room temperature and have high ionic conductivity and are compatible with polymer membranes.

In this study, we have developed an IL redox flow battery chemistry that involves the use of a 1:1 e+/e- IL redox couple. The ILs are based on EMI cations and TEA anions with a 1:1 e+/e- stoichiometry. These ILs are liquid at room temperature and have high ionic conductivity and are compatible with polymer membranes.

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The surfaces of heterogeneous catalysts in reactive environments are dynamic and require in situ characterization studies under reaction conditions to fully understand their fundamental structure-activity relationships. This presentation will focus on the application of Raman spectroscopy to determine the nature of the catalytic active sites in different reaction environments. Emphasis will be placed on investigating heterogeneous supported metal oxide catalysts containing multiple catalytic active sites and determining the roles of each of the sites. Some of the examples to be presented will be the metathesis of H2=CH=CH2 to H2=C=CH2 and H2=C=CH=CH2 by supported ReOx/Al2O3 catalysts, polymerization of H2=C=CH2 by supported Cr2O5/α-Al2O3 and methanol conversion to aromatic liquids by supported MoOx/ZSM-5 catalysts.

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

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

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This talk describes the design and operation of a nanoindentation instrument that is widely used in the study of the mechanical deformation of materials on small length scales (~ micrometer). Raman spectroscopy is a technique that provides insights into the interplay between mechanical stresses involved in the mechanical deformation of materials, such as strain build-up, phase transformations and variations in crystallinity. Typically these approaches have been used separately wherein the spectroscopic analysis of the material might take place prior to and after the end of a mechanical transformation. Of course, there is significant interest in in situ analyses of materials during mechanical transformation as such an approach promises a richer understanding of the underlying physics than is likely possible with analysis limited to pre- and post-transformation. For example, the ability to follow the path of phase transformations rather than just the endpoints is certainly desirable. Consequently, significant effort has been directed toward the coupling of indentation instruments with various in situ analysis capabilities.
Dynamic Processes of Single Atoms and Molecules at Surfaces

Playing host to the first-of-its-kind Symposium: Single Atoms and Molecules at Surfaces, the afternoon session features the Invited Talk: Transition to Reversible Spin Control, Individual Functional Molecules: from Reversible Conductance to Reversible Spin Control, presented by Hong-Jun Gao.

**Moderator:** Arthur Utz, Tufts University, Andrew Gellman, Carnegie Mellon University

8:00am SS+AS+EN-WeM1 Construction and Manipulation of Individual Functional Molecules: from Reversible Conductance Transition to Reversible Spin Control. Hong-Jun Gao, Chinese Academy of Science, China

Control over charge and spin states at the single molecule level is crucial not only for a fundamental understanding of charge and spin interactions but also represents a prerequisite for development of molecular electronics and spintronics. While charge manipulation has been demonstrated by gas adsorption and atomic manipulation, the reversible control of a single spin of an atom or a molecule has been challenging. In this talk, I will present a demonstration about a robust and reversible spin control of single magnetic metal-phthalocyanine molecule via attachment and detachment of a hydrogen atom, with manifestation of switching of Kondo resonance. Low-temperature atomically resolved scanning tunneling microscopy was employed. Using density functional theory calculations, the spin control mechanism was revealed, by which the reduction of spin density is driven by charge redistribution within magnetic 3d orbitals rather than a change of the total number of electrons. This process allows spin manipulation at the single molecule level, even within a close-packed molecular array, without concern of molecular spin exchange interaction. This work opens up a new opportunity for quantum information recording and storage at the ultimate molecular limit.

References:

*In collaboration with Liwei Liu, Kai Yang, Yuqiang Jiang, Boqun Song, Wende Xiao, Linfei Li, Haitao Zhou, Yeliang Wang, and Shixuan Du, Institute of Physics, Chinese Academy of Science, Beijing 100190, China

8:40am SS+AS+EN-WeM3 Single Molecule Origins of Electronic Disorder: Random Conformations of α-NPD Molecules on Au(111). Daniel Dougherty, J. Wang, J. Wang, North Carolina State University

Disorder is an important aspect of modeling organic and polymeric electronic materials. Proper accounting of the effects of disorder both in active layers and at interfaces with contacts determine the detailed current-voltage characteristics in organic thin film devices [1]. Our study seeks to visualize and statistically quantify the disorders in α-NPD films at the single molecule scale. This molecule is a common hole transport material in spectroscopy to observe numerous surface structures of active layers and at interfaces with contacts determine the detailed current-voltage characteristics. Using STM and temperature atomically resolved scanning tunneling microscopy was employed. Using density functional theory calculations, the spin control mechanism was revealed, by which the reduction of spin density is driven by charge redistribution within magnetic 3d orbitals rather than a change of the total number of electrons. This process allows spin manipulation at the single molecule level, even within a close-packed molecular array, without concern of molecular spin exchange interaction. This work opens up a new opportunity for quantum information recording and storage at the ultimate molecular limit.

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9:00am SS+AS+EN-WeM4 Pt-Cu Single Atom Alloys for the Selective Partial Hydrogenation of Butadiene. Felicia Lucci, M. Marsinkowski, E. C. Arad, Tufts University

Butene is a common feedstock for polymerization reactions; however, butadiene is a minority impurity that poisons the polymerization catalyst. The selective hydrogenation of butadiene to butene serves to increase the purity of the feedstock without reducing the overall concentration of butene. Therefore, catalysts that selectively hydrogenate butadiene to butene and prevent the hydrogenation of butene to butane are of great interest. Using scanning tunneling microscopy and spectroscopy to observe numerous surface structures of α-NPD on the (111) surface of Au. These structures are distinguished by different lateral order as well as different local molecular conformations. Random molecular conformations on the surface lead to an statistical distribution of hole transport states that is consistent with the distribution inferred from device analysis.

9:00am SS+AS+EN-WeM4 Pt-Cu Single Atom Alloys for the Selective Partial Hydrogenation of Butadiene. Felicia Lucci, M. Marsinkowski, E. C. Arad, Tufts University

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9:40am SS+AS+EN-WeM5 Toward a Dynamical Understanding of Chemistry at Metal Surfaces. Alec Wodtke, Max Planck Institute for Biophysical Chemistry

One of our most fundamental scientific challenges is to develop predictive theories of chemistry rigorously grounded in the laws of physics. In 1929, Dirac identified the problem famously in a comment about the importance of quantum mechanics to chemistry: “The underlying physical laws necessary for the mathematical theory of... the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.” Despite electrifying advances in computational power, Dirac is still right. The theory of chemistry requires approximate methods for practical computations.

For the theory of surface chemistry, three central approximations are made, involving the use of: 1) classical mechanics for describing nuclear motion, 2) density functionals for calculating electronic states and the Born-Oppenheimer approximation to separate electronic and nuclear degrees of freedom.

The growing importance of computational surface chemistry motivates us to design rigorous experimental tests of these assumptions. Many fundamental questions arise. Can we trust the Born-Oppenheimer approximation for calculating potential energy surfaces for reactions at metal surfaces? Can we characterize and overcome the weaknesses of density functional theory, for example by developing new wave-function based methods for the solid-state? For all of these reasons, it is important to carefully design experimental tests of the capabilities of modern computational surface chemistry.

Using modern molecular beam methods in state-to-state scattering experiments, we obtain a wealth of observational data characterizing the interactions of molecules with metal surfaces. Emphasizing quantitative comparison to first principles theories, we find that energy conversion can occur by unexpected mechanisms, where the electronically adiabatic approximation separating the time scales of electronic and nuclear motion is found to be invalid. The simplicity of the systems under study provides opportunities for developing new theories that go beyond the Born-Oppenheimer approximation. One important outcome of this is the realization that Born-Oppenheimer breakdown can be induced by simple electron transfer events that are common in surface chemistry.

10:10am SS+AS+EN-WeM6 Steric Effect in O2 Chemisorption on Al(111). Mitsuomi Kurahashi, Y. Yamauchi, National Institute for Materials Science (NIMS), Japan

O2 adsorption on Al(111) has been investigated intensively as the most representative system of the dynamical process happening on the surface, however, remained unclear. An STM study by Brune et al.[1] has proposed that adsorbed O-atoms are atomic and are well separated each other. Initially, this has been ascribed to the transitive mobility driven by the O2 chemisorption energy (“hot-atom” mechanism)[1], but this mechanism has been found to be unlikely. The abstraction mechanism, in which one O-atom is bound to the surface while the other is ejected, has been proposed alternatively based on the resonance enhanced multi-photon ionization measurement.[2] It is however not evident whether or not the abstraction process is the dominant event at low translational energies (E0). In addition, the STM study by Schmid et al.[3] has suggested that the adsorbates consist of two O-atoms locating at nearby sites. This cannot be explained by the abstraction mechanism.

In this study, we focused attention to the alignment dependence in the O2 sticking, the anisotropy and reaction mechanism. A single spin-polarized state-selected [(LM) (2,2)] O2 beam, for which we can specify both the molecular alignment and spin direction relative to the magnetic field, was adsorbed on an Al(111) surface. The results show that O2 molecules parallel to the surface have much higher sticking probabilities than those perpendicular to the surface at E0 = 0.2 eV. The E0 dependence of the sticking probability indicates that the dissociation barrier at the perpendicular geometry is smaller than 0.1 eV higher than the parallel geometry. The present results reveal that the abstraction process, which occurs at the perpendicular geometry, is a minor event at low E0.[4]

References:
Recent transition state and quantum dynamics calculations have suggested an important role for surface atom motion in promoting methane dissociation on transition metals including Ni, Pt, and Ir. Here, we describe state-resolved gas-surface scattering measurement of methane dissociation on Ni(111), Ir(111), and Ir(110)-(1x2). Infrared laser excitation prepares a single molecule rotational and vibrational state at a well-defined internal energy. A supersonic molecular beam provides tight control over the translational energy of the methane molecules. The methane molecules, with their well-defined energy, accentuate the role of surface temperature, and the resulting thermal motion of surface atoms, on reactivity.

The presentation will focus on recent experimental results. On the Ir(110)-(1x2) surface, we observe both precursor-mediated and direct reaction channels for the vibrationally excited \((v_\text{eq}=0)\) molecules to temperatures 100 and 300K on the Ir(110) surface. We will also report on more recent studies that explore the surface temperature dependence of more highly vibrationally excited methane molecules.

11:04am SS+AS+EN-WeM12 Activation of \(C_2H_6\) Alkanes on Pt(111): Importance of Dynamics, van der Waals Interactions, and Gas-Surface Energy Transfer
Jason Navin, B.S. Donald, K. G. Ching, I. A. Harrison, University of Virginia

A variety of dissociative sticking coefficients (DSCs) were measured for alkanes varying in size from methane to nonane on Pt(111) using an effusive molecular beam technique. Thermal equilibrium \((T_g = T_s)\) and non-equilibrium \((T_g \neq T_s)\) DSC measurements provided information about the gas-surface reactivity and energy transfer. Angle-resolved DSCs, \(S(700 \text{ K}, \theta)\), measured for methane, ethane, and propane on Pt(111) were used to define thermal DSCs, \(S(T_g)\), and discern dynamical behavior. Methane and ethane DSCs were sharply peaked around the surface normal and were found to have similar dynamical biases away from statistical behavior. Precursor-mediated microcanonical trapping (PMMT) models were used to both analyze and predict DSCs over a wide range of experimental conditions and experiments. It was found that the activation energy for dissociative chemisorption on an alkane scales linearly with its molecular desorption energy from the physisorption well in front of the surface. The molecular desorption energy should be proportional to the van der Waals stabilization energy for the products of dissociative chemisorption. The gas-surface energy transfer increased as the alkane size increased from \(C_1\) to \(C_9\). For alkanes larger than \(C_5\), the gas-surface energy transfer was apparently sufficient to fully thermalize the impinging molecule to the temperature of the surface before reaction such that, \(S(T_g=300\text{K},T_g) = S(T)\).

12:00pm SS+AS+EN-WeM13 Shining light on an Important Intermediate Step in Photocatalysis: Probing Polaron in \(ZnO\) using Infrared Reflection Absorption Spectroscopy,
Fabian Behensee, H. Sezen, Karlsruhe Institute of Technology, Germany, A. Nefedov, C. Wöll, Karlsruhe Institute of Technology

ZnO is a wide-bandgap metal oxide exhibiting various highly desirable physical and chemical properties, among them high photocatalytic activity. As such, it has been widely studied employing virtually all available techniques over the past 50 years. In the context of photoexcitations, primarily such, it has been widely studied employing virtually all available techniques over the past 50 years. In the context of photoexcitations, primarily excited \((v_\text{eq}=1)\) molecules to temperatures 100 and 300K on the Ir(110) surface. We will also report on more recent studies that explore the surface temperature dependence of more highly vibrationally excited methane molecules.

8:20am SS+AS-WeM2 The Role of Time-scale Analysis in Simulation of ALD and CVD Surface Reaction Kinetics, Raymond Adomaitis, E. Remmers, C. Travis, D. Arana-Chavez, University of Maryland, College Park

In this paper, we will describe our research on the mathematical structure of atomic layer deposition (ALD) and chemical vapor deposition (CVD) surface reaction kinetics models. Our primary objective is to investigate the mathematical structure of the differential-algebraic (DAE) systems of equations describing surface reaction species dynamics during these thin-film deposition processes. The research is motivated by the challenges presented by writing a well-posed DAE model for surface reaction species dynamics as well as the difficulties encountered when numerically solving these systems. Using a perturbation analysis approach, we demonstrate that the deposition kinetics decomposes naturally into slow (deposition reactions), fast (equilibrium reactions), and instantaneous (conserved quantities) time scales. A key contribution of our work is the development of a reaction network factorization procedure that partitions the surface reaction and deposition species dynamic balances into the distinct time scale ranges described. Under what conditions this procedure works, understanding the implications of fixed points for dynamic ALD processes, interpreting reaction fluxes, and extending the methods to spatially distributed processes in the context of representative thin-film application domains will be discussed. Physical interpretation of DAE system initial conditions for these surface processes constitutes another important research direction in this project; results will be presented which illuminate alumina ALD growth surface dynamics at the start of each exposure (TMA and water) and purge period.
Formic acid (HCOOH) is a simple molecule that is an abundant product of biomass processing and can serve as an internal source of hydrogen for oxygen removal and upgrading of biomass to chemicals and fuels. In addition, HCOOH and its derivatives can be used as a fuel for low temperature fuel cells. We present a systematic study of the HCOOH decomposition reaction mechanism starting from first-principles and including reactivity and microkinetic modeling. In particular, periodic self-consistent Density Functional Theory (DFT) calculations are performed to determine the stability of reactive intermediates and activation energy barriers of elementary steps. Pre-exponential factors are determined from vibrational frequency calculations. Microkinetic models developed and calculated reaction rates and reaction orders are then compared with experimentally measured ones. These comparisons provide useful insights on the nature of the active site, most-abundant surface intermediates as a function of reaction conditions and feed composition. Trends across metals on the fundamental, atomic-scale level up to selectivity trends will be discussed. Finally, we identify from first-principles alloy surfaces, which may possess better catalytic properties for selective dehydrogenation of HCOOH than monometallic surfaces, thereby guiding synthesis towards promising novel catalytic materials.

We review previous results for using the capture-zone [island proximity cell] distribution (CZD) in island growth to extract information about the critical nucleus size. Over the experimentally accessible region, the CZD is well described by the generalized Wigner distribution \( P_D(\gamma) = a_0 \delta^{\beta-\beta_D} \), dependent only on the exponent \( \beta \). For diffusion-limited aggregation (DLA), \( \beta = i/2 \). We discuss recent experimental applications. For comparison with this approximate conceptual correlation, the dependence of the growth exponent \( \gamma \) (stable island density \( N \rightarrow \infty \), where \( F \) is the flux) for both DLA and attachment-limited aggregation (ALA). In either case, \( \chi \beta = i \), so that for ALA, where \( \chi = 2/(i+3) \), we find \( \beta = (i+3)/2 \). We compare with experiments depositing pentacene (5A) and p-hexaphenyl (6P) on sputtered mica.

Furthermore, recent experiments studying 5A on amorphous mica give evidence of nucleation via a hot precursor state, with an unusual relation between \( N \) and \( t \). For attachment-limited aggregation (ALMA), we examine a model of such behavior. We use rate equations and Walton's relation. We take deposited monomers to be hot initially, traveling ballistically with temperature-independent speed \( v \) until a time \( t \), when they thermalize. For the dimensionless combination \( z = v t / N^{1/2} \ll 1 \) rapid thermalization occurs, with consequent DLA nucleation. For \( z \gg 1 \) we find the precursor behavior for hot-monomer aggregation (HMA): \( \chi = 1 \), unexpectedly, the same form as for ALA. We scrutinize behavior in both limits as well as in the crossover regime \( z \sim 1 \), in which behavior can be described using an effective \( \chi \). At low temperatures, the behavior becomes markedly non-Arrhenius, insensitive to temperature. We conclude a discussion of more general applications of this framework.

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validated interatomic potential, Ge deposition and islanding on an amorphous SiO$_2$ surface is studied with direct molecular dynamics and the results are compared to experimental measurements [4] of island size distributions as a function of deposition rate and temperature. A key aspect of our modeling approach is a procedure to accelerate the simulations. While direct molecular dynamics simulations of Ge deposition on SiO$_2$ are able to capture Ge island nucleation, growth and coarsening, the very fast deposition rates necessary make difficult direct comparison to experimental measurements of island density and size distributions. In particular, we show that direct molecular dynamics simulations are able to approach, but not quite reach, the deposition conditions in experiment. The accelerated simulations are based on “equation-free” coarse projective integration [5]. Here, measures of the island size distribution dynamics are obtained from short molecular dynamics simulations and then used to evolve numerically the size distribution over large time intervals. The new island size distribution is then used to reconstruct consistent atomic configurations that are subsequently evolved further with molecular dynamics and the process is repeated. Here, we show that the reconstruction of atomic configurations from size distribution moments represents the key challenge in deposition simulations and we propose approaches for achieving this in a computationally tractable manner.


12:00pm SS+AS-WeM13 Dimerization Induced Deprotonation of Water on RuO$_2$(110), R. Mu, D.C. Cantu, V.-A. Glezakou, Z. Wang, I. Lyubinetsky, R. Rosseau, Zdenek Dohnalek, Pacific Northwest National Laboratory

RuO$_2$ has proven to be indispensable as a co-catalyst in numerous systems designed for photocatalytic water splitting. Here we present a first mechanistic study of water adsorption, dissociation, and diffusion on the most stable RuO$_2$ surface, rutile RuO$_2$(110). Variable temperature scanning tunneling microscopy (STM) and ab initio molecular dynamics based density functional theory calculations (DFT) are employed to follow the behavior of small water clusters. We show that water monomers adsorb molecularly on Ru sites, become mobile above 240 K, and diffuse along the Ru rows. The monomers readily pair up and form dimers that are immobile below 273 K. Finally, the dimers deprotonate and form Ru-bound H$_2$O-OH and bridging OH species. This is in a sharp contrast with the molecular binding of water dimers observed on isostructural TiO$_2$(110). The onset for diffusion of H$_2$O-OH pairs on RuO$_2$(110) is observed at ~273 K, indicating a significantly higher diffusion barrier than that for water monomers. The experimentally determined diffusion barriers are in agreement with those obtained from the DFT calculations. The diffusion of H$_2$O-OH pairs is found to proceed via a rollover mechanism, with a water molecule moving over OH, followed by hydrogen transfer from H$_2$O to OH. At high water coverages, water dimers are found to be the building blocks of longer water chains on Ru rows. The observed behavior of water monomers and dimers is compared and contrasted with that previously reported on isostructural rutile TiO$_2$(110).
Monolayer molybdenum disulfide (MoS\(_2\)) is a two-dimensional crystal comprising a single layer of molybdenum atoms sandwiched between two layers of sulfur atoms. Monolayer MoS\(_2\) differs from its celebrated all-carbon cousin, graphene, by the presence of a direct band gap leading to robust light absorption and by strong electron-electron interactions leading to formation of rightly bound excitons. In this talk, we demonstrate that both electrical and optical properties of MoS\(_2\) can be widely tuned via external influences.

In the first part of the talk, we study changes in the bandgap and phonon spectra in strained MoS\(_2\). We investigate the transition from direct to indirect band gap in MoS\(_2\) under uniaxial strain. The experimental signatures of this transition include strain-induced changes in the PL wavelength and intensity.

Second, we examine the influence of the environment of MoS\(_2\) on its properties. We demonstrate substrate-induced scattering is suppressed in suspended MoS\(_2\) specimens. We use photocurrent spectroscopy to study excitations in pristine suspended MoS\(_2\). We observe band-edge and van Hove singularity excitons and estimate their binding energy. We study dissociation of these excitons and uncover the mechanism of their contribution to photoresponse of MoS\(_2\).

3:00pm 2D+AS+EM+MI+MN+NS+TF-WeA3 Electron-Phonon Coupling and Photoluminescence in Single Layer Transition Metal Dichalcogenides, Neha Nayyar, V. Turkowski, D.T. Le, T.S. Rahman, University of Central Florida. Single layer MoS\(_2\) and other transition metal dichalcogenides have been the subject of numerous investigations because of their unusual optical, electronic and transport properties. To understand and thereby tune their photoluminescent properties, we have analyzed the role of electron-phonon interactions. Density functional perturbation theory is used to calculate the dispersion of system phonons, while electron-phonon coupling is obtained using the Eliashberg approach. Time-dependent density-functional theory based calculations using the density-matrix approach is employed to study the exciton and trion excitations which are found to appear as peaks in the absorption spectrum in the visible range with binding energy ~0.5 – 1 eV and ~0.02-0.03 eV, correspondingly. The emission peak is found to also lie in the visible spectrum and is sensitive to the value of the electron-phonon coupling, which depends on the nature and extent of doping. The position of the spectral peaks may thus be manipulated by doping. Calculations of the self-energy and spectral functions of doped systems show excitations to have 10-100 fs lifetime, which makes the system interesting for ultrafast applications. Comparison will be made of these optical properties of several single layer dichalcogenides and contact will be made with available experimental data. Work supported in part by DOE Grant No. DOE-DE- FG02-07ER46354.

3:20pm 2D+AS+EM+MI+MN+NS+TF-WeA4 Temperature Dependent Photoluminescent Spectroscopy of MoS\(_2\), Michael Watson, J.R. Simpson, Towson University & NIST, R. Yan, H. Xing, University of Notre Dame, S. Bertolazzi, J. Brivio, A. Kis, EPFL, Switzerland, A.R. Hight-Walker, NIST.

We report temperature and power dependent photoluminescent (PL) of molybdenum disulfide (MoS\(_2\)). Mechanical exfoliation of bulk MoS\(_2\) from bulk provides single-layer flakes which are then transferred either to substrate substrates or suspended over holes in Si/Si 3 N 4. We measure temperature dependence from ~100K to 400K and power dependence from ~6mW to ~7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main excitonic peak(A) at ~1.87eV which consist of both neutral excitons and charged trions (A\(^-\) or A\(^+\)) [1]. The A\(^-\) excitons peak and the A\(^+\) exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE, a broad peak centred at ~1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

Notre Dame

Room: 310 - Session 2D+AS+EM+MI+MN+NS+TF-WeA

2:20pm 2D+AS+EM+MI+MN+NS+TF-WeA1 Tuning Excitons in Two-Dimensional Semiconductors, Kirill Botolin, Vanderbilt University

We report temperature and power dependent photoluminescence (PL) of molybdenum disulphide (MoS\(_2\)). Mechanical exfoliation of MoS\(_2\), from bulk provides single-layer flakes which are then transferred either to substrate substrates or suspended over holes in Si/Si 3 N 4. We measure temperature dependence from ~100K to 400K and power dependence from ~6mW to ~7mW using an Argon laser at 514.5nm and a HeNe laser at 632.8 nm. The PL spectrum exhibits a main excitonic peak(A) at ~1.87eV which consist of both neutral excitons and charged trions (A\(^-\) or A\(^+\)) [1]. The A\(^-\) excitons peak and the A\(^+\) exciton peak redshift and broaden with increasing temperature and power. Along with the A peak, we observe a lower energy bound exciton (BE) that is likely related to defects. The BE, a broad peak centred at ~1.7eV, linearly redshifts and narrows with increasing power. The power dependence of both the main and bound peak saturates above 0.5mW. Raman temperature and power dependence will also be discussed [2].

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2H-TaS\(_2\) and 1T-TaS\(_2\), and 1T-TaSe\(_2\). In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-conducting phases, and a phase transition at a critical temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2H-TaS\(_2\) and 1T-TaS\(_2\), and 1T-TaSe\(_2\), carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.

4:00pm 2D+AS+EM+MI+MN+NS+TF-WeA8 Few-Layer and Symmetry-Breaking Effects on the Electrical Properties of Ordered CF\(_3\)Cl Phases on Graphene. Josue Morales-Cifuentes, T.L. Einstein, Y. Wang, J. Reut-Robey, University of Maryland, College Park.

An effective potential mechanism for breaking the inherent sublattice symmetry of graphene has been studied using DFT calculations on hexagonal boron nitride.\(^1\) Electrical detection of CF\(_3\)Cl phase transitions on graphene shows the existence of a commensurate ordered phase in which this can be tested.\(^2\) We study the electronic properties of similar phases varying coverage and orientation of CF\(_3\)Cl with respect of the graphene substrate using VASP ver 5.3.3, with ab initio van der Waals density functionals (vdW-DF\(^1\), vdw-DF\(^2\)).\(^3\) Consistent with a physisorbed phase, binding energies are calculated to be on the order of 290meV, and insensitive to coverage and orientation of the CF\(_3\)Cl molecules. Charge transfer was calculated to be sensitive with coverage, but not orientation, which is qualitatively consistent with experiment. For low coverages, sub-lattice symmetry breaking effects are responsible for gap openings in the order of 4meV, whereas for large coverages it is the formation of ordered overlayers that opens gaps of 15meV. Furthermore, in bilayer graphene at low coverage we estimate an enhanced gap of 20meV.

\(^1\) Gianluca Giovannetti et al., PRB 76, 073103(2007)

\(^2\) Yilin Wang et al., APL 103, 201606(2013)

\(^3\) Jiri Klimes et al., PRB 83, 195131(2011)

\(^4\) Kyuo Lee et al., PRB 82, 081101(R)(2010)

5:00pm 2D+AS+EM+MI+MN+NS+TF-WeA9 Optical Anisotropies in Layered Nanomaterials. Jon Schuller, UC Santa Barbara

In nanomaterials optical anisotropies reveal a fundamental relationship between structural and optical properties. In layered materials, optical anisotropies may result from in-plane and out-of-plane dipoles associated with intra- and inter-layer excitations respectively. In this talk, I describe a novel method wherein we resolve the orientation of luminescent excitons and isolate photoluminescence signatures from distinct intra- and inter-layer excitations, respectively. We compare photoluminescence anisotropies in materials with weak or strong interlayer coupling, MoS\(_2\), and the organic semiconductor PTCDA respectively. We demonstrate that photoluminescence from MoS\(_2\) mono-, bi- and trilayers originates solely from in-plane excitons, whereas PTCDA supports distinct in-plane and out-of-plane exciton species with different spectra, dipole strengths and temporal dynamics. The insights provided by this work are important for understanding fundamental optical properties in layered nanomaterials and designing optical systems that efficiently excite and collect light from exciton species with different orientations.

4:20pm 2D+AS+EM+MI+MN+NS+TF-WeA7 Effects of Dimensionality on the Raman and Photoluminescence Spectra of TaS\(_2\) and TaSe\(_2\) Dichalcogenides, Danilo Romero, University of Maryland, College Park, M. Watson, J.R. Simpson, Towson University, H. Berger, Ecole Polytechnique Federale de Lausanne, Switzerland, A.R. Hight Walker, NIST.

We investigate the effects dimensionality on the electronic properties through the optical spectra of the transition-metal dichalcogenides 2H-TaS\(_2\) and 1T-TaSe\(_2\), and 1T-TaS\(_2\). In bulk, these materials exhibit electronic states from Mott insulator, commensurate and incommensurate charge-conducting phases, and a phase transition at a critical temperature. We explore the evolution of these properties as the materials approach a few layers, achieved via mechanical exfoliation of bulk single-crystals. Raman and photoluminescence spectroscopy of 2H-TaS\(_2\) and 1T-TaSe\(_2\), and 1T-TaS\(_2\), carried out over a wide-range of temperature, were used as a probe of the change of the electronic properties from the bulk to single-layer phases of the materials. Comparison of the phonon and excitonic transitions as a function of temperature and dimensionality will be presented.
on both pristine and polycrystalline samples of 2D materials, while being successful in measuring overall mechanical performance of graphene, require some theoretical input to extract the important mechanical properties. Large-scale atomistic molecular dynamics simulations are used to predict the mechanical properties of 2D materials, such as the elastic modulus, breaking strength, stress/strain distributions, and mechanisms of fracture under conditions of AFM nanoindentation experiments. Perfect, defective, and polycrystalline samples are investigated using large-scale molecular dynamics simulations with a screened environment-dependent bond order (SED-REBO) potential. The mechanisms of crack propagation in both perfect and defective samples will also be presented.

6:00pm 2D+AS+EM+MI+MN+NS+TF-WeA12 Mechanical Control of Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers. Evan Reed, K.-A.N. Duerloo, Y. Li, Stanford University.

Mo- and W- dichalcogenide compounds have a two-dimensional monolayer form that differs from graphene in an important respect: it can potentially have more than one crystal structure. Some of these monolayers exhibit tantalizing hints of a poorly understood structural metal-to-insulator transition with the possibility of long metastable lifetimes. If controllable, such a transition could bring an exciting new application space to monolayer materials beyond graphene. Here we discover that mechanical deformations provide a route to switching the thermodynamic stability between a semiconducting and a metallic crystal structure in these monolayer materials. We employ density functional and hybrid Hartree-Fock/density functional calculations including vibrational energy corrections to discover that single layer MoTe2 is an excellent candidate phase change material. We identify a range from 0.3% to 3% for the tensile strains required to transform MoTe2 under uniaxial conditions at room temperature. We elucidate the appropriate thermodynamic constraints for monolayers, which can differ from bulk materials. The potential for mechanical phase transitions is predicted for all six studied compounds. The potential application space ranges from catalysis to information storage and nanoscale electronics.

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

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

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

X-ray photoelectron spectroscopy (XPS) is demonstrated as a quantitative surface analysis technique which can be used to determine the type of corrosion chemistry that occurs. Stainless steel (316L) substrates containing 70% Fe, 18% Cr, 8% Ni and 2% Mo (as well as a low concentration of impurities) are suspended in water at 300 °C for 1000 hours. A metal oxide double layer is found to develop over time on the stainless steel surface: the top layer is a mix of magnetite (Fe3O4) and Nickel Ferrite (NiFe2O4) and the bottom layer is a mix of magnetite and chrome (FeCr2O4) (below is the base metal).

A high energy, medium sized argon gas cluster source is shown to be advantageous compared to a conventional monatomic argon ion source when depth profiling such layered structures, causing reduced structural and chemical damage from the ion beam sputtering process. Data acquisition at small analysis areas gives well resolved spectra, revealing the multi-layered oxide structures produced from the corrosion process.


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

This study focuses on the application of time-of-flight SIMS (TOF-SIMS), with supporting XPS analysis for quantification, to determine the molecular decomposition and metal-organic reaction products of lubricants used in bio-diesel fuel. The test specimens were produced on a reciprocating cylinder-on-flat tribometer to simulate the piston / cylinder contact geometry and dynamics that are typical of internal combustion engines. The lubricant used in the bio-diesel fuel consists of C18 fatty acids at a concentration in the high part-per-million (ppm) range. The TRIFT mass spectrometer of the PHI nanoTOF provides an advantage for this study in that the wear track topography is effectively decoupled from the molecular characterization and imaging. The HR' imaging mode of the PHI nanoTOF, simultaneously achieving a spatial resolution < 400 nm and a mass resolution ≈ 10,000 is an important asset in molecular identification and imaging.

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

INVITED

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

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

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

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

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

Using surface analysis has been a mainstay of industrial research and corporate analytical labs for more than thirty years. The applications of surface chemical analysis in an industrial setting range from the investigation of the composition and chemistry of buried interfaces of single molecule memory devices created in the R&D lab to the routine analysis of plasma treated polymer surfaces on the production line. Some analyses are performed to provide a 'yes' or 'no' answer to question such as 'Has the oxide been removed?' or 'Was the surface plasma treated?'. Other analyses are performed to provide more detailed information and often require the application, and correlation of several analytical methods. This correlation between techniques often occurs in the characterization of, for example, fab processes where a process may be characterized by x-ray photoelectron spectroscopy to understand the chemistry; but then the analysis needs to correlate to the information obtained by Auger electron spectroscopy or ToF SIMS which are the techniques of choice when the process is scaled to dimensions where XPS is not practical. Further, simple data processing such as calculating atomic concentrations, is often not the end of the analytical study. Examples of using numerical methods such as linear least squares fitting or the application of Tougaard backgrounds to clarify an analysis will also be discussed. More detailed analyses can also be achieved by applying modeling methods such as SESSA or using simple overlay models to describe a material. This presentation will cover these different aspects of surface chemical analysis in an industrial laboratory with practical examples of using XPS, AES and ToF SIMS for process characterization, materials development and failure analysis.

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

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

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

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

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

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

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

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

Energy Frontiers Focus Topic Room: 315 - Session EN+AS+EM-WeA

Organic-Inorganic Interfaces for Energy
Moderator: Ramana Chintalapudi, University of Texas at El Paso

2:20pm EN+AS+EM-WeA1 Towards Efficient Solution Processed Organic Photovoltaic Devices, E. Reichmanis, Georgia Institute of Technology

INVITED Solution-processed π-conjugated semiconductors exhibit potential in the development of low-cost, light-weight and large-area flexible plastic optoelectronics, particularly photovoltaics (OPVs). However, one drawback to current OPVs is their limited efficiency. We have explored the use of donor-acceptor (D-A) hybridization to tailor HOMO/LUMO energy levels and thus the band gap. Materials exhibiting high charge carrier mobility and strong low-energy absorption profiles have been synthesized and characterized. Coupled with materials structure, the performance of devices fabricated using polymeric semiconductors depends critically upon alignment of the polymer chains at the nano- through meso- and macro-scales. Significant structure-process-property relationships that allow for enhancement of long-range order will be discussed. For instance, a lyotropic liquid crystalline (LC) phase has been observed in poly-(3-hexylthiophene) (P3HT) with very high order and can lead to large improvement. The lessons learned through these studies may allow for simple, controllable, and cost-effective methodologies for achieving high performance flexible plastic electronic devices.
We have used time-resolved terahertz spectroscopy (TRTS) to measure lifetimes and determine recombination mechanisms in Cu2ZnSn(S,Se)4 (CZTS) thin films fabricated from nanocrystal inks. TRTS probes photoconductivity on femtosecond to nanosecond time scales that are relevant to the recombination in thin film photovoltaics. Terahertz frequencies (0.2–2.5 THz) correspond to typical scattering rates in semiconductors, enabling consideration of carrier density and mobility. Ultrafast time resolution permits tracking the evolution of carrier density to determine recombination mechanisms. By manipulating the photoexcitation wavelength and fluence, we can tailor the generation profile of photocreated carriers to distinguish between surface, Shockley-Read-Hall (SRH), and Auger recombination mechanisms and the dominating recombination process. TRTS experiments and modeling were used to understand the role of recombination mechanisms and their contribution to photovoltaic performance. TRTS photocconductivity shows an instrument-limited onset within 1 ps of an ultrafast pump pulse, followed by a slow decay over nanoseconds. Photoconductivity decay kinetics were fit with a biexponential model with two time constants and a weight fraction, ~0.8. TRTS is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the probe wavelength. As the excitation wavelength is tuned from blue to red, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

3:00pm EN+AS+EM-WeA3 Understanding Carrier Dynamics in Cu2ZnSn(S,Se)4 Using Time-Resolved Terahertz Spectroscopy, G. W. Giuglietta, Drexel University, K. Roy Choudhury, J. V. Caspar, DuPont Central Research and Development, Jason Baxter, Drexel University. We have used time-resolved terahertz spectroscopy (TRTS) to measure lifetimes and determine recombination mechanisms in Cu2ZnSn(S,Se)4 (CZTS) thin films fabricated from nanocrystal inks. TRTS probes photoconductivity on femtosecond to nanosecond time scales that are relevant to the recombination in thin film photovoltaics. Terahertz frequencies (0.2–2.5 THz) correspond to typical scattering rates in semiconductors, enabling consideration of carrier density and mobility. Ultrafast time resolution permits tracking the evolution of carrier density to determine recombination mechanisms. By manipulating the photoexcitation wavelength and fluence, we can tailor the generation profile of photocreated carriers to distinguish between surface, Shockley-Read-Hall (SRH), and Auger recombination mechanisms and the dominating recombination process. TRTS experiments and modeling were used to understand the role of recombination mechanisms and their contribution to photovoltaic performance. TRTS photocconductivity shows an instrument-limited onset within 1 ps of an ultrafast pump pulse, followed by a slow decay over nanoseconds. Photoconductivity decay kinetics were fit with a biexponential model with two time constants and a weight fraction, ~0.8. TRTS is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the probe wavelength. As the excitation wavelength is tuned from blue to red, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

5:00pm EN+AS+EM-WeA9 Engineering Exciton Recombination in Organic Light-Emitting Devices, Russell Holmes, University of Minnesota. While capable of realizing very high peak efficiency, many organic light-emitting devices (OLEDs) suffer a significant reduction in efficiency under large injected current densities. This efficiency roll-off can limit device brightness and potentially compromise operational stability. Much previous work has identified the key contributing factors to the efficiency roll-off in phosphorescent OLEDs. Through the use of a bi-emissive (D-EML) and tri-emissive (G-EML) anode architecture, many of these losses are identified and recombination at the surface. The long time constant is typically ~2 ns and is attributed to SRH recombination. Assignment of these mechanisms is supported by the dependence of kinetics upon excitation fluence and wavelength. Normalized kinetics are independent of fluence over a range of 40x, indicating that no Auger recombination is occurring. Without Auger recombination, we can distinguish between surface and SRH rates by tuning the probe wavelength. As the excitation wavelength is tuned from blue to red, carriers are generated nearer to the front surface and the photoconductivity kinetics are sensitive to the surface recombination velocity. With blue excitation, we see that a larger fraction, ~0.5, of carriers recombine with a short time constant. With redder excitation wavelengths, the carriers are generated more evenly throughout the film and the kinetics are dominated by SRH recombination with the long time constant having a majority of the weight fraction, ~0.8. TRTS provides a pathway to determine performance-limiting recombination mechanisms and measure key parameters like SRH lifetime and surface recombination velocity, helping to direct the design of efficient thin film photovoltaics.

5:40pm EN+AS+EM-WeA11 Interface Engineering to Control Magnetic Field Effects of Organic-based Devices by using a Self-assembled Monolayer, Hyuk-Jae Jang, NIST & WPU, S.J. Poopkpratana, NIST, A.N. Brigeman, Wake Forest University, J.V. Kline, NIST, J.J. Busham, NIST, R. Dandlikach, C.A. Hacker, O.A. Kirillova, NIST, O.D. Jurchescu, Wake Forest University, C.A. Richter, NIST. Magnetic field effects (MFEs) in non-magnetic organic semiconductors provide a non-contact approach to control electronic and optoelectronic properties of organic-based devices by using a sub-tesla magnetic field and thus they have been of great interest to industry as well as academia around the world. However, the understanding of MFEs has been hindered due to the lack of systematic studies. In this work, we present comprehensive studies on the correlation between MFEs in organic-based devices and the field dependence of magnetic properties of organic semiconductors. Magnetic field effects (MFEs) in organic-based devices have been known for their versatile use in various technological applications. In this presentation, we report a novel method of manipulating the MFEs on electrical resistance of organic semiconductor devices, namely organic magnetoresistance in Alq3 (tris-(8-hydroxyquinoline) aluminum) – based devices by simply adding a molecular self-assembled monolayer (SAM) between a metal electrode and an organic semiconductor. SAMs have been known to alter the bulk properties of their corresponding substrates, such as the dielectric constant and work function. In particular, SAMs can alter the physical property of an inorganic solid surface and thus modify the interface between an electrode and an organic thin film when a SAM is inserted between them. We show for the first time that the interfacial modification by simply inserting a fluorinated SAM (heptadecafluoro-l-decanethiol [CF7(CF)7(CH2)17SH]) or F-SAM in organic-based devices changes the sign of organic magnetoresistance due to the change in relative strength of different MFE mechanisms existing in organic-based devices. In addition, we utilize different MFE mechanisms coexisting in organic-based devices by adding a thin TPD (N,N′-bis(3-methylphenyl)-N,N′-diphenylbenzilidine) layer to create a system whose organic magnetoresistance can be tuned by an external bias voltage. References


6:00pm EN+AS+EM-WeA12 Study on the Correlation between Electrode-Active Layer Interfaces and Performance of Polymer Solar Cells, Xuansin Ju, J.F. Zhu, University of Science and Technology of China. The PSCs were fabricated with different cathodes (Ca/Al and Al) as the active layers. The PSCs were fabricated with different cathodes (Ca/Al and Al) as the active layers.
The Ca/Al interlayer significantly improves the open circuit voltage (VOC), short circuit current (JSC), fill factor (FF) so as to improve the PCE in comparison with Al as the cathode. In order to understand how the electrodes affect the device performance, the Ca/PCDTBT and AI/PCDTBT interfaces were investigated by transient photovoltage (TPV), charge extraction (CE) and synchrotron radiation photoemission spectroscopy (SRPES). The TPV and CE measurements were used to determine the charge carrier lifetime and density. Charge carrier recombination rate constant was found to be much smaller in the device with Ca/Al cathode as compared to that with AI cathode. Energy band diagrams and interfacial chemical reactions were characterized using high-resolution SRPES. The results indicate that the Ca interlayer can induce the stronger dipole moment, which facilitates electrons collection and drives holes away at the cathode/polymer interface. The device performance was improved because of the lower recombination.

### Nanometer-scale Science and Technology

**Room: 304 - Session NS+AS-WeA**

**Nanoscale Imaging and Materials Characterization**

**Moderator:** Craig Prater, Anasys Instruments, Paul Sheehan, Naval Research Laboratory


**INVITED**

Despite that nanodiamond (ND) particles were discovered more than 50 years ago and were mass produced in the early 80s, for a long time they were in the shadow of their more famous sp² carbonous. Two recent major breakthroughs, production of individual 4-5nm particles and particles containing colour centres exhibiting stable luminescence and unique spin properties have brought ND particles to the forefront of materials research.¹ Nanometer size particles are produced by detonation of carbon-containing explosives or by grinding of microdiamond powders. Besides well-known outstanding mechanical and thermal properties, diamond particles have remarkable optical properties in combination with biocompatibility, high specific surface area, and tuneable surface structure. Applications of ND which have captivated the imagination of scientists in areas which have broad societal impact, such as energy preservation and biomedical imaging, will be briefly illustrated and a more in-depth review of their optical properties provided.

The optical emission, scattering and attenuation of ND are finding unique applications. In life sciences nanoparticles are increasingly used as fluorescent probes to monitor cellular interactions and study cellular dynamics at the single molecular level. Foreign atoms can be incorporated into the lattice of ND particles providing photostable particles as well as systems for quantum sensing that may be used to probe the intracellular environment at the molecular scale. Development of multimodal imaging probes based on 5-10nm ND and doping of ND with different elements to generate photoluminescent ND is increasingly being viewed as a means of drug delivery. Encapsulating ND in a porous silica shell is a means of achieving stable fluorescent imaging with nanoparticles with a high loading capacity for bioactive molecules.

Due to its high refractive index, wide bandgap and crystalline lattice, ND highly attenuates and scatters ultraviolet radiation. High attenuation and scattering in combination with large surface area has been shown as a means of increasing the radiation resistance of polymer nanocomposites. This can be beneficial in sunscreens as well as in polymers used in the construction of satellites to be placed in low Earth orbit.


3:00pm **NS+AS-WeA3 Oxidation State Sensitive Imaging of Ceria Nanoparticles, Aaron Johnston-Peck, National Institute of Standards and Technology (NIST)**

Scanning transmission electron microscopy (STEM) coupled with electron energy loss spectroscopy (EELS) has been successfully applied to track changes to composition as well as bonding environment with atomic resolution. These measurements impose exacting experimental and instrumentation requirements include aberration-corrected optics, electron sources with narrow energy spreads, and extremely stable room environments. Therefore it seems prudent when possible that other techniques with less demanding experimental requirements supplement EELS measurements. Imaging or diffraction techniques greatly relax these aforementioned requirements as the need for corrective optics and narrow energy monochromators can be eliminated. The drawback of the induced artifacts is reduced because the total electron dose needed to form an image or diffraction pattern is less than an EELS spectrum image. Low angle annular dark field (LAADF) STEM is presented as an alternative to EELS measurements to identify changes to local changes of oxidation state in ceria (CeO₂) nanoparticles. This relationship was established through the use of EELS, in-situ measurements, and image simulations. Ceria has numerous energy related applications due to the ability of ceria to store and release oxygen. The formal charge of the cerium ions transition from 4+ to 3+ as oxygen vacancies are formed. These oxygen vacancies cause local distortions to the crystal and subsequently produces additional diffuse scattering to low angles. The LAADF STEM signal is sensitive to this change in scattering and contrast variations in the image become resolved. Additionally, preliminary experiments on other metal oxide nanoparticles suggest that this approach may be applied to other material systems and processes as well.

3:20pm **NS+AS-WeA4 Shape and support interaction of size-selected Pd and Pt NPs on TiO₂(110), Mahdi Ahmad, F. Behafarid, University of Central Florida, B. Roldan Cuenya, Ruhr-University Bochum, Germany**

The shape and the support interaction of 3D palladium and platinum nanoparticles (NPs) deposited on TiO₂(110) was investigated using scanning tunneling microscopy (STM). The NPs were synthesized using inverse micelle encapsulation. In spite of the initial random location of the micelle-prepared NPs on the support, step edge decoration was observed after annealing at high temperature (>1000°C). In general, the resolving of the shape of 3D NPs using STM is very challenging due to the tip-convolution effects. However, a combination of ultra-sharp STM tips and samples containing structurally well-defined NPs allowed us to resolve the NP shape, with the highest features on the NPs being unaffected by tip artifacts. It was found that all NPs had a truncated octahedron shape, with [111] top and interfacial facets. Furthermore, the alignment of the NP edges (or symmetry axes) with the TiO₂(110)-[001] atomic rows evidenced the epitaxial relationship with support achieved after annealing. The STM data were analyzed following the Wulff-Kaischew theorem, and a MATLAB code was used to reconstruct the NP shape, eliminating overestimations in the lateral size inherent to the STM technique due to tip effects. The surface energy ratio γ₁₀/₀/₁₁ was calculated for each Pd NP with an average value of 1.12±0.07, which is in good agreement with theoretical values. Moreover, the adhesion energy was found to display a size-dependence, with larger NPs having smaller adhesion energy. This phenomenon can be explained based on the minimization of the interfacial area by reducing the contact area. Following similar analysis on Pt NPs on TiO₂(110), a higher γ₁₀/₀/₁₁ ratio of 1.18±0.1 was obtained as compared to Pd. Also, the rate of decrease in the adhesion energy with increasing NP height was lower for Pd as compared to Pd.

4:20pm **NS+AS-WeA7 Nanoscale Imaging and Spectroscopy of Plasmonic Hot Spots and Dark Modes with the PTIR Technique, Andrea Centrone, National Institute of Standards and Technology (NIST)**

**INVITED**

Localized surface plasmon resonances couple propagating light with nanoscale volumes of matter (hot-spots), enabling new applications in sensing and therapeutics. Surface-Enhanced Infrared Absorption (SEIRA) Spectroscopy exploits such hot-spots for sensitive chemical detection. Calculations predict large SEIRA enhancement factors but the diffraction of long IR wavelengths (2 μm - 16 μm) has hindered the experimental determination of SEIRA enhancement with nanoscale resolution.

Photo Thermal Induced Resonance (PTIR) combines the chemical specificity of IR spectroscopy with the lateral resolution of Atomic Force Microscopy (AFM). PTIR circumvents the limitations of light diffraction by employing an AFM tip as a local detector for measuring the transient thermal expansion induced by the absorption of light pulses in the sample. Local IR spectra and composition maps are obtained recording the amplitude of the tip deflection as a function of the laser wavelength and position, respectively. Notably, the PTIR signal is proportional to the absorbed energy (not scattering) and the PTIR spectra are directly comparable with IR spectral libraries, enabling materials identification.

In this work, the PTIR technique is applied to image the dark plasmonic resonance of gold Asymmetric Split Ring Resonators (A-SRRs) in the mid-IR with nanoscale resolution. Additionally, the chemically-specific PTIR
signal is used to map the local absorption enhancement of PMMA coated A-SRRs, revealing hot-spots in the resonators’ gaps with enhancement factors of $S > 30$.

The local information gathered with in the PTIR experiments can provide insightful information and possibly help to engineer nanomaterials for greatest efficiency. As an additional example the PTIR technique will be applied to image phase separated domains in Metal-Organic Frameworks single crystals, a novel class of materials that find application in catalysis, sensing and separation.

5:00pm NS+AS-WeA9 AFM-based Infrared Spectroscopy—Nanoscale Chemical Analysis with Sensitivity Down to Single Monolayers. Craig Prater, K. Kjoller, M. Lo, E. Dillon, R. Shetty, Anasys Instruments, C. Marcott, Light Light Solutions, F. Lu, M. Jin, M. Belkin, University of Texas at Austin, A. Dazzi, Université Paris-Sud, France

The ability to perform chemical analysis at the nanoscale has been considered one of the “holy grails” of the scanning probe microscope community. Many techniques have been developed to provide material contrast in SPM images based on a variety of properties (electronic, optical, mechanical, etc.), but there had not been the ability to perform broadly applicable chemical analysis on diverse samples. We have developed AFM-based infrared spectroscopy (AFM-IR) that enables broadly applicable chemical analysis on samples with nanoscale spatial resolution and with sensitivity down to the scale of individual molecular monolayers. The AFM-IR technique illuminates a sample with light from a tunable infrared laser source and then uses the tip of an AFM to measure the sample’s local photothermal expansion due to the absorption of infrared light at specific wavelengths. Measuring absorption as a function of wavelength creates an IR absorption spectrum that acts as a chemical fingerprint to characterize and identify chemical components. Mapping IR absorption spatially over a sample at different wavelengths can be used to create maps of nanoscale chemical composition. Recently we have implemented two techniques to extend both the applicability and sensitivity of the AFM-IR technique. First, we implemented top side illumination to enable AFM-IR on a much wider array of samples and sample substrates. Second, we developed a resonance enhanced mode where the IR laser pulses are synchronized to a contact resonance of the AFM cantilever. Combined with “lightning rod” enhancement of the incident IR light, the resonance enhanced technique can achieve chemical analysis with single monolayer sensitivity and spatial resolution ~25 nm. We will describe the AFM-IR technique, recent innovations and applications in materials, life sciences, photonics, and semiconductors.

References:

5:20pm NS+AS-WeA10 Schottky Barrier Height Mapping of Nanoengineered Metal/ Semiconductor Interfaces. Robert Balsamo, C. Durcan, University of Albany-SUNY, A. Matsubayashi, V.P. LaBella, University at Albany-SUNY

Metal-semiconductor junctions form rectifying contacts known as Schottky diodes, which have an energy barrier determined by charge transfer and bonding at the interface. Current-voltage and capacitance-voltage spectroscopy measurements yield a spatially averaged barrier height. Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM) technique that can measure transport of hot electrons through materials and interfaces locally with high spatial and energetic resolution due to the precise positioning of the STM tip. This presentation details work done to map the Schottky barrier height with nanoscale resolution at several metal/semiconductor interfaces. These maps can give insight into the homogeneity of the barrier height as well as the spatial distribution of individual metal species. Potentially this technique can be used to image nanoeengineered interfaces.

5:40pm NS+AS-WeA11 Scanning Electron Microscopy to Probe Electron Transport of Working Nanodevices under Realistic Operation Conditions. Ana Stevanovic, A. Kolmakov, National Institute of Standards and Technology (NIST)

The interplay between the electron transport and chemical status of the surface of working nanodevices can be affected by local electroactive inhomogeneities (defects), presence of near surface depletion regions and Schottky contacts. In spite of tremendous progress achieved in understanding of semiconductor chemical sensors, very little experimental data are available on aforementioned interplay in working devices under realistic operation conditions. Ambient pressure electron microscopy is used in this work to address in situ imaging of a formation of electroactive inhomogeneities inside SnO$_2$ nanowire device as a function of gas environment and temperature under realistic operating conditions. In addition, using scanning photoelectron and Auger microscopy with the lateral resolution of ca 80 nm, we are able to access spectroscopically the fine changes in surface condition of an individual SnO$_2$ nanowire during their operation. It is possible to monitor the changes in a conductance of the SnO$_2$ nanodevice in operando mode upon exposure to different redox gases and relate them to the formation of the specific surface groups.

Scanning Probe Microscopy Focus Topic Room: 312 - Session SP+AS+B1+NS+SS-WeA

Advances in Scanning Probe Microscopy
Moderator: Tae-Hwan Kim, Pohang University of Science and Technology, Jewook Park, Oak Ridge National Laboratory

2:20pm SP+AS+B1+NS+SS-WeA1 Majorana Mode in Vortex core of Bi$_2$Te$_3$/NbSe$_2$Topological Insulator-Superconductor Heterostructure. Jinfeng Jia, Shanghai Jiao Tong University, China

Majorana fermions have been intensively studied in recent years for their importance to both fundamental science and potential applications in topological quantum computing. Majorana fermions are predicted to exist in a vortex core of superconducting topological insulators, however, they are extremely difficult to be distinguished experimentally from other quasiparticle states for the tiny energy difference between Majorana fermions and these states, which is beyond the energy resolution of most available techniques. Here, we overcome the problem by systematically investigating the spatial profile of the Majorana mode and the bound quasiparticle states within a vortex in Bi$_2$Te$_3$/NbSe$_2$ by using in situ ultralow temperature STM/STS. While the zero bias peak in local conductance splits right off the vortex center in conventional superconductors, it splits off at a finite distance ~20nm away from the vortex center in Bi$_2$Te$_3$/NbSe$_2$, primarily due to the Majorana fermion zero mode. While the Majorana mode is destroyed by reducing the distance between vortices, the zero bias peak splits as a conventional superconductor again. This work provides strong evidences of Majorana fermions and also suggests a possible route to manipulating them.

References:

* In cooperation with Jin-Peng Xu, Mei-Xiao Wang, Zhi Long Liu, Jian-Feng Ge, Xiaojuan Yang, Canhua Liu, Zhu An Xu, Dandan Guan, Chao Lei Gao, Dong Qian, Ying Liu, Qiang-Hua Wang, Fu-Chun Zhang, Qi-Kun Xue

3:00pm SP+AS+B1+NS+SS-WeA3 Robust Protection from Backscattering in the Topological Insulator Bi$_2$Sb$_2$Te$_3$/Se$_3$$_1$. Fumio Komori, S. Kim, S. Yoshizawa, Y. Ishida, University of Tokyo, Japan, K. Eto, K. Segawa, Osaka University, Japan, S. Shin, University of Tokyo, Japan, Y. Ando, Osaka University, Japan

Three-dimensional (3D) topological insulators (TIs) are accompanied by gapless surface states due to a nontrivial $Z_2$ topology of the bulk wave functions. The topological surface state (TSS) of a 3D TI is helically spin polarized, which leads to a suppression of electron scatterings due to spin mismatch between the eigenstates before and after the scattering. The suppression has been inferred from the measurements of quasiparticle interference (QPI) using scanning tunneling microscopy. No QPI was observed for intraband scatterings within unwarped TSSs. However, it has not been clear to what extent the scattering is suppressed within TSS. In the present study, we have elucidated how the elastic scattering is suppressed as a function of the scattering angle and electron energy in the helicity-spin-polarized surface electrons in a single and unwarped upper Dirac cone of Bi$_2$Sb$_2$Te$_3$/Se$_3$$_1$. In this material [1], $E_F$ is located very close to the Dirac energy $E_D$. We compared the scattering wave vectors observed at $E_F$ with the diameters of the constant-energy contours of the unoccupied TSS which was measured by using time-resolved ARPES implementing a pump-probe method. Moreover, the inelastic scattering time of unoccupied TSS was directly obtained by this method.
At the energy above \( E_D \), we found that there is a sharp threshold for the length of the scattering vector, above which the observed QPI intensity is abruptly diminished. Such a threshold indicates the existence of a well-defined critical scattering angle beyond which elastic scattering is suddenly suppressed. The observed protection from backscattering in the TSS occurs not only for 180° but also for a wide range of angles between 100° and 180°. Such a wide angle range for the protection from backscattering is found to be essentially independent of the energy up to 300 meV above \( E_D \), until the Dirac cone becomes warped and the bulk scattering events intervene. At energies higher than 300 meV, we found hexagonal patterns in the FT-QPI images that come from warping of the TSS Dirac cone. In this energy range, the critical scattering vector was not clearly observed, indicating a different mechanism of the protection from backscattering in the warped Dirac cone. The observed inelastic scattering lifetime of TSS is longer than 15 ps just above \( E_D \). The robust protection from the backscattering and long inelastic scattering in the TSS strongly support the possible applications for electronics and spintronics using weak electron scattering of TSS at \( E_D \).

References

4:20pm SP+AS+BI+NS+SS-WeA7 Direct Observation of Edge States of 1D and 2D Topological insulators, Han Young Yeom, Institute for Basic Science, Republic of Korea

At the energy above \( E_D \), we found that there is a sharp threshold for the length of the scattering vector, above which the observed QPI intensity is abruptly diminished. Such a threshold indicates the existence of a well-defined critical scattering angle beyond which elastic scattering is suddenly suppressed. The observed protection from backscattering in the TSS occurs not only for 180° but also for a wide range of angles between 100° and 180°. Such a wide angle range for the protection from backscattering is found to be essentially independent of the energy up to 300 meV above \( E_D \), until the Dirac cone becomes warped and the bulk scattering events intervene. At energies higher than 300 meV, we found hexagonal patterns in the FT-QPI images that come from warping of the TSS Dirac cone. In this energy range, the critical scattering vector was not clearly observed, indicating a different mechanism of the protection from backscattering in the warped Dirac cone. The observed inelastic scattering lifetime of TSS is longer than 15 ps just above \( E_D \). The robust protection from the backscattering and long inelastic scattering in the TSS strongly support the possible applications for electronics and spintronics using weak electron scattering of TSS at \( E_D \).

References

4:20pm SP+AS+BI+NS+SS-WeA7 Direct Observation of Edge States of 1D and 2D Topological insulators, Han Young Yeom, Institute for Basic Science, Republic of Korea

Invited

1D and 2D topological insulators (TI's) are characterized by 0D and 1D edge states of exotic spin-charge characteristics. In this talk, we introduce the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact and the nanoscale Scanning Tunneling Microscopy on MoS\(_2\), MoS\(_2\)-xSe\(_2\), and MoSe\(_2\) Monolayer Islands and Films Grown by CVD, Velveth Klee, D. Barroso, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bartels, E. Velveth, E. Preciado, University of California - Riverside, J. Mann, L. Bar
Nanostructures including 2D Heterostructures, Patterning of 2D Materials
Moderator: Kirill Boltotin, Vanderbilt University

8:00am 2D+AS+HI+NS+SS-ThM1 Stitching and Stacking for Atomically Thin Circuity. Jiooong Park, Cornell University INVITED
The development of large scale growth methods based on chemical vapor deposition (CVD) has enabled production of single-atom-thick films with diverse electrical properties, including graphene (conductor), h-BN (insulator), and MoS2 (semiconductor). Precise vertical stacking and lateral stitching of these 2D materials will provide rational means for building ultrathin heterostructures with complex functionality. However, large scale production and control of these structures requires new characterization and fabrication approaches. In this talk, I will first discuss the structure and physical properties unique to CVD graphene in single and bilayers. Using the atomic-resolution imaging as well as a dark-field transmission electron microscopy (TEM) technique, our group investigated the structure of grain boundaries in CVD graphene and its impact on the mechanical, electrical, and chemical properties. This allowed us to produce CVD graphene with optimized electrical properties. We also reported a new patterned regrowth method to fabricate 2D lateral heterojunctions entirely made of graphene and h-BN, which enables the development of atomically thin integrated circuitry. If time allows, I will also discuss our recent results on the large scale growth of high quality single layer MoS2 as well as graphene film with a uniform lattice orientation. Our characterization and growth approach would ultimately allow the fabrication of electrically isolated active and passive elements embedded in continuous, one-atom-thick sheets, which could be manipulated and stacked to form complex devices at the ultimate thickness limit.

8:40am 2D+AS+HI+NS+SS-ThM3 Vertical and Lateral Heterostructures of Carbon Nanomembranes (CNMs) and Graphene. Andreas Winter, University of Bielefeld, Germany, M. Woszczyna, R. Stosch, T. Weimann, F. Ahlrels, Physikalisch-Technische Bundesanstalt, Germany, A. Turchanin, University of Bielefeld, Germany
Heterostructures of graphene with other 2D materials are of great interest for nanoscience and nanotechnology. However, their fabrication is still not a trivial task. Here we present the engineering and characterization of (i) vertical and (ii) lateral heterostructures of molecular thin (~1 nm) dielectric carbon nanomembranes (CNMs) made of aromatic molecules [1] and single-layer (SLG) graphene sheets. (i) The vertical CNM/SLG heterostructures with terminal amino-groups (NH2) are assembled via the single-layer (SLG) graphene sheets. (ii) Precise vertical stacking and lateral stitching of these 2D materials will provide rational means for building ultrathin heterostructures with complex functionality. However, large scale production and control of these structures requires new characterization and fabrication approaches. In this talk, I will first discuss the structure and physical properties unique to CVD graphene in single and bilayers. Using the atomic-resolution imaging as well as a dark-field transmission electron microscopy (TEM) technique, our group investigated the structure of grain boundaries in CVD graphene and its impact on the mechanical, electrical, and chemical properties. This allowed us to produce CVD graphene with optimized electrical properties. We also reported a new patterned regrowth method to fabricate 2D lateral heterojunctions entirely made of graphene and h-BN, which enables the development of atomically thin integrated circuitry. If time allows, I will also discuss our recent results on the large scale growth of high quality single layer MoS2 as well as graphene film with a uniform lattice orientation. Our characterization and growth approach would ultimately allow the fabrication of electrically isolated active and passive elements embedded in continuous, one-atom-thick sheets, which could be manipulated and stacked to form complex devices at the ultimate thickness limit.

The isolation of graphene and the subsequent reports on its electronic properties have spurred tremendous interest in a variety of two dimensional (2D) materials for electronic device applications. Layered semiconducting transition metal dichalcogenides (TMDs) of Mo and W have emerged as promising alternatives to graphene for optoelectronic applications due to their finite band gap in the visible portion of the electromagnetic spectrum.1 The atomically thin structure of these 2D materials coupled with van der Waals bonding between adjacent layers allows their stacking into atomically sharp heterostructures with defect-free interfaces, in contrast to epitaxially grown III-V semiconductor heterostructures where the material choices are constrained by lattice matching. Additionally, the few atom thickness of the individual layers enables doping modulation of the overlying layers in a heterostructure using a global back gate. While a large number of heterostructure devices employing graphene have been reported, it’s gapless band structure prevents the formation of a large potential barrier for charge separation and current rectification. Consequently, a p-n heterojunction diode derived from ultrathin materials is notably absent and significantly constrains the fabrication of complex electronic and optoelectronic circuits. Here we demonstrate a gate-tunable p-n heterojunction diode using semiconducting single-walled carbon nanotubes (SWCNTs) and single-layer molybdenum disulphide (SL-MoS2) as atomically thin p-type and n-type semiconductors, respectively. The vertical stacking of these two direct band gap semiconductors forms a heterojunction with electrical characteristics that can be tuned with an applied gate bias over a wide range of charge transport behavior, ranging from insulating to rectifying with forward-to-reverse bias current ratios exceeding 106. In addition, the gate-dependent characteristics of this diode exhibit a unique ‘anti-ambipolar’ behavior with two off-states at either extremes of the gate voltage range and a maximum on-state current current between them. This heterojunction diode also responds to optical irradiation with photoresponse time < 15 μs.2 We anticipate that the novel properties and characteristics of this p-n heterojunction can be widely generalized to other atomically thin materials systems.

REFERENCES:
have considered different periodicities among layers to reduce as far as possible the incommensurability between lattices. Our results show that BN bare layers fit into the intrinsic stacking structure of isolated SiC, and the d<sub>0</sub>-d<sub>2</sub> gap remains proximately unchanged. Graphene and silicene severely modify the electronic structure introducing additional states within the optical gap. Adsorption on graphene produces that the system turns like a zero band gap semiconductor bringing the conduction bands of MoS2 down to the Fermi level of graphene. Adsorption on silicene shifts both valence and conduction bands of MoS2, towards the Fermi level of silicene, in addition to inducing a gap of about 50 meV in the silicene itself. This work was partially supported by CONACYT (México) Postdoctoral Fellowship Program (number 204065) and DOE grant DE-FG02-07ER46354

11:00am 2D+AS+HI+NS+SS-ThM10 Ballistic Transport in Epitaxial Graphene Nanoribbons, Walt de Heer, Georgia Institute of Technology INVITED

Graphene nanoribbons are essential components in future graphene nanoelectronics. However, in typical nanoribbons the electronic property is determined by the lithographically patterned exfoliated graphene, the charge carriers travel only about 10 nanometers between scattering events, resulting in minimum sheet resistances of about 1 kΩ In contrast 40 nm wide graphene nanoribbons that are epitaxially grown on silicon carbide are single channel room temperature ballistic conductors on greater than 10 μm length scales, similarly to metallic carbon nanotubes. This is equivalent to sheet resistances below 1Ω surpassing theoretical predictions for perfect graphene by at least an order of magnitude. In neutral graphene ribbons, we show that transport is dominated by two modes. One is ballistic and temperature independent; the other is thermally activated. Transport is protected from back-scattering, possibly reflecting ground state properties of neutral graphene. At room temperature, the resistance of both modes abruptly increases non-linearly with increasing length, one at a length of 16 μm and the other at 160 nm. Besides their importance for fundamental science, since epitaxial graphene nanoribbons are readily produced by the thousands, their room temperature ballistic transport properties can be used in advanced nanoelectronics as well.

11:40am 2D+AS+HI+NS+SS-ThM12 Solution-Synthesized Graphene Nanoribbons, Alexander Sinitskii, University of Nebraska - Lincoln

In this talk I will discuss a recently developed bottom-up approach for gram quantities of narrow graphene nanoribbons that are less than 2 nm wide and have atomically precise armchair edges. These graphene nanoribbons have been characterized by a number of microscopic (STM, AFM, SEM, TEM) and spectroscopic (XPS, UPS/IPES, UV-vis-NIR, IR and Raman spectroscopy) techniques. The properties of graphene nanoribbons could be tuned by incorporation of nitrogen atoms in armchair edges. Narrow graphene nanoribbons have a large electronic bandgap, which makes them promising for applications in field-effect transistors with high on-off ratios, as well as bulk applications, including coatings, composites and photovoltaic devices.

12:00pm 2D+AS+HI+NS+SS-ThM13 Graphene Silicon Interfaces at the Two-Dimensional Limit, Brian Kiraly, A.J. Mannis, M.C. Hersam, Northwestern University, N.P. Guisinger, Argonne National Laboratory

Artificial van der Waals heterostructures have demonstrated both significant improvements of graphene's intrinsic properties and entirely new properties of their own. Early interest in these structures was based on nearly ideal periodicity 6.4 Å; Raman spectroscopy reveals peaks at 520 cm<sup>-1</sup> and 900-1000 cm<sup>-1</sup> that coincide precisely with bulk diamond cubic silicon, indicating these domains are comprised of sp<sup>2</sup> bonded crystalline Si. These 2D sheets of silicon demonstrate both semiconducting character and a honeycomb lattice. These structures have been selected for a silver-based reconstruction of the Si(111) surface. The resulting silicon domains grow in two different configurations with respect to the dendritic graphene: (1) silicon domains appear to grow directly on the Ag(111) surface and terminate at the graphene boundaries. These in-plane interfaces are atomically-precise and clearly resolved via scanning tunneling microscopy. Electronically, the density of states of both isolated substrate and layer persist to these interfaces within the resolution of the measurement, indicating little interaction at the border. (2) The silicon growth is observed underneath the existing graphene flakes. The vertically stacked silicon graphene domains are identified via atomically resolved imaging through the graphene domains at larger biases where graphene is transparent under STM. Furthermore, the vertical materials interfaces demonstrate distinct electronic signatures from either constituent material. The resulting interfaces represent atomically pristine interfaces between graphene and a sp<sup>2</sup> bonded semiconducting Si film, demonstrating a significant step forward in the diversification of van der Waals heterostructures.

Atom Probe Tomography Focus Topic

Room: 301 - Session AP+AS+MC+NS+SS-ThM

APT Analysis of Semiconductors, Magnetic and Oxide Materials

Moderator: Paul Bagot, Oxford University, UK, Daniel Perea, Pacific Northwest National Laboratory

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

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

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

CuIn(Ga)Se<sub>2</sub> (CIGS), CuZnSnSe<sub>2</sub> (CZTSe), and multicrystalline Si (mc-Si) solar cells possess a high efficiency [1], despite the polycrystalline structure of the absorber layer. One of the major factors controlling the cell efficiency is the diffusion of the impurities during the fabrication process into the absorber layer and to the p-n junction [2]. However, the interaction between the defects and the impurities at the internal interfaces is not completely understood. This is due to a lack of information on the local chemical changes across the internal interfaces at the nanoscale. As a step towards a better understanding of the impurity redistribution at the internal interfaces, we have developed novel approaches of preparing site-specific atom probe specimens using combined focused ion beam (FIB), (scanning) transmission electron microscopy (STEM) and electron backscattered diffraction (EBSD). These approaches allow selected GBs in polycrystalline CIGS, CZTSe and mc-Si layers to be studied by atom probe tomography (APT).

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

The microstructure and chemistry of a permanent magnet... by HRTEM precipitating Sm2(Co,Fe)17Bx (2:17:x) magnetic phases were confirmed using both shape during the APT analysis. In this work we utilized laser assisted APT materials. The recent (theoretical) discovery that in high fields the band gap semiconductors with regard to local fields inside and on the surface of such summarizing the theoretical results for Atom Probe Tomography of metallic... APT+AS+MC+NS+SS-ThM13 Detector Dead-time Effects on the Accurate Measurement of Boron in Atom Probe Tomography. Frederick Meisenkothen, National Institute of Standards and Technology (NIST), T.J. Prosa, CAMECA Instruments Inc., E.B. Steel, R.P. Kolli, University of Maryland, College Park

The atom probe tomography (APT) instrument uses a time-of-flight (TOF) mass spectrometer to identify ions that are field ionized and evaporated from the apex of a needle-like nano-tip specimen. A pulse event, either laser or voltage, is used to trigger field evaporation and to initiate the timing sequence for the mass spectrometer. Ideally, a single atom is field evaporated during a single pulse event. However, it is also common to have multi-hit detection events where more than one ion strikes the detector between pulses. For reasons not completely understood, some elements, such as boron, are prone to field evaporation in multi-hit detection events when compared to other elements, and a large fraction of the boron signal is reportedly lost during acquisition. Obtaining an improved understanding of the field evaporation behavior of boron at different concentration levels, in view of the limited ability of the detection system to resolve multi-hit detection events, may lead to new ways to compensate for the boron signal loss. A nominally pure boron sample was chosen as a high boron concentration material while the boron implanted silicon, NIST-SRM2137, (1E15 atoms cm⁻² retained dose) was chosen as the low boron concentration material.

A dual-beam FIB/SEM instrument, with an insitu lift-out system, was used to prepare the APT specimen tips from the bulk materials. A laser pulsed LEAP 4000X S* instrument was used to acquire APT data sets for each of the specimen tips. Custom software scripts were used to filter the data sets and extract the ion information associated with specific search criteria, e.g. event multiplicity, which is the number of ions within a given multi-hit event. Ion correlation analysis was used to graphically demonstrate the detector dead-time effect. In the present work, more than 60% of the detected boron signal resides within the multi-hit detection events, for both the high and low boron concentration samples.

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

Spectroscopic Ellipsometry Focus Topic

8:00am EL+AS+EM+EN+SS-ThM Spectroscopic Ellipsometry for Photovoltaics and Instrument Development

Moderator: Mariadriana Creatore, Eindhoven University of Technology, Netherlands, Tino Hofmann, University of Nebraska-Lincoln

INVITED

Thin film large area photovoltaics (PV) are a maturing field, yet challenges remain in manufacturing and fundamental research. Even the simplest thin film PV devices consist of multiple layers of doped or undoped semiconductors, transparent conducting front contacts, and metal back contacts. Characteristics of each layer, along with the interfaces between layers, all have an impact upon device performance. Within each layer, the material may evolve with thickness or exhibit spatial non-uniformity. Furthermore, studies of each thin film material can be difficult, as fundamental property measurements on special substrates may not accurately represent the characteristics of the material in the final device configuration. Spectroscopic ellipsometry (SE) data, collected over the infrared to ultraviolet, is sensitive to layer thicknesses, interface formation, and surface roughness as well as the optical response of each component in the form of the complex dielectric function spectra (ε = ε₁ + iε₂) for samples deposited on arbitrary reflective substrates. Variations in e for a given layer can be linked to order (amorphous vs. crystalline, grain size, crystal phase), composition, and characteristics of opto-electronic response (band gap, dc electrical properties). In situ real time SE (RTSE) is now often applied to

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study the growth evolution of component materials within device configurations for hydrogenated silicon (Si:H), cadmium telluride (CdTe), and copper indium gallium diselenide (CIGS) thin film solar cells. In-situ spectroscopic ellipsometry (SE) is a non-invasive tool for monitoring material properties and allows for the real-time analysis of glass/TCO-stack/CdS/O/CdTe solar cells in the superstrate configuration.

For the solar cells, CdS:O layers with different oxygen contents were deposited on 15 cm x 15 cm TCO coated glass superstrates. A 16 x 16 array of dot cells each with an area of 0.125 cm² was fabricated on the superstrate in order to optimize efficiency improvements through combinatorial methods. The as-deposited superstrate/substrate-structure undergoes additional processing steps during device fabrication, three sets of TG-SE mapping data sets were analyzed based on an optical model deduced from RT-SE studies of the CdS:O/CdTe superstrate. The results of this analysis assist in the development of a realistic optical model for the multilayer structure of the solar cell. Using this optical model ex-situ through-the-glass spectroscopic flattening (TG-SE) has been implemented for the analysis of glass (TCO-stack)/CdS/O/CdTe solar cells in the superstrate configuration.

8:40am **EL+AS+EM+EN+SS-ThM3** Application of Pseudo-Bulk Approach in Ellipsometric Studies of Polycrystalline Photovoltaic Thin Films, Sukheen Choi, National Renewable Energy Laboratory, J. L. University of Toledo, I. Repins, National Renewable Energy Laboratory, Ohio, U.S.

Fundamental band gap is one of the key properties of semiconducting materials, which directly influences the functionality and performance of many photonic and photovoltaic (PV) devices. Photoluminescence (PL) and optical absorption spectroscopies are widely used to determine the band-gap energy \( E_g \). For polycrystalline thin-film PV materials, however, it is often challenging to unambiguously interpret PL data owing to the presence of multiple peaks associated with various defects and disorder in the film. To estimate \( E_g \) from optical absorption spectrum, on the other hand, a straight segment of the absorption coefficient curve needs to be chosen. But this selecting procedure is somewhat arbitrary, which leads to an inaccurate \( E_g \) value.

Spectroscopic ellipsometry (SE) accurately determines material’s optical function spectra over a wide spectral range. For semiconductor thin-film structures, a multilayer analysis is generally used to extract the optical information from each individual layer. Although multiple defects associated with various defects and disorder in the film. To estimate \( E_g \) from optical absorption spectrum, on the other hand, a straight segment of the absorption coefficient curve needs to be chosen. But this selecting procedure is somewhat arbitrary, which leads to an inaccurate \( E_g \) value.

To reduce complications in mathematical modeling of SE data and improve the accuracy of results, near-band-gap optical function spectra, we introduce the pseudo-bulk approach, where SE measurements are performed on thin films grown on macroscopically roughened substrate surface. The essence of this approach is in suppressing the reflection of probing light from the film/substrate interface and below. Thus, no thickness fringes appear in the SE data, despite the thin film nature of sample, and the band-gap energy \( E_g \) can be obtained from the growth curve of \( \tan \psi \) vs. \(1/\lambda^2 \). To correct for SE data well-above the band gap in the analysis, several contributions should be considered for those near (and below) the band gap, such as the optical characteristic of substrate, presence of interfacial layers, and finite thickness of film in addition to the artifacts from surface overlayers. As a result, the obtained optical function spectrum and \( E_g \) value become somewhat model dependent with an increased uncertainty.


In-situ real-time spectroscopic ellipsometry (RT-SE) has been applied for the analysis of CdS:O layers sputter deposited on C-Si substrates from a C advantages of the as-deposited plasma employed for the deposition. Tracking the time dependence of both film and plasma properties is desirable as variations in material properties resulting from changes in plasma conditions may impact the final device performance. In this particular study, we look at the growth evolution of semiconductor, transparent conducting oxide (TCO), and metal contact layers commonly used in thin film photovoltaic devices. Case studies involve undoped, n-type, and p-type hydrogenated amorphous silicon prepared by PECVD, as well as zinc oxide, indium tin oxide, and silver prepared by magnetron sputtering on either smooth test substrates (glass, crystal silicon wafers) or in the full device configuration. Variations in thin film structural conditions (bulk layer thickness, surface roughness) and optical properties in the form of the complex dielectric function spectra \( \epsilon = \epsilon_1 + \epsilon_2 \) are obtained as a function of time by RT-SE. Parameters from RTSE \( \epsilon \) structures are interpreted to determine order of magnitude (grain size, amorphous vs. nanocrystalline), electronic transitions (band gap, free carrier absorption characteristics), and morphology evolution as appropriate for the given material layer. OES indicates the presence and relative strength of plasma emission peaks, which correspond to the species present in the plasma and their relative concentrations. Analysis of RTSE and OES data collected simultaneously is sought to identify links present between these plasma and film characteristics.

9:40am **EL+AS+EM+EN+SS-ThM6** Optical Insights into Graphene Functionalized by Atoms, Biomolecules and Metal Nanoparticles, Maria Losurdo, M. Giangregorio, G.V. Bianco, P. Capezzuto, G. Bruno, CNR-IMIP, Italy

New opportunities for energy production and storage, catalysis, biosensing, drug delivering and plasmonics are offered by graphene-based materials. In order to make all those applications viable technologies, it is mandatory to functionalize graphene for modulating reproducibly its properties and for better understanding the surface and interfacial electronic phenomena in graphene hybrids.

To this aim, this contribution discusses the optical properties measured by spectroscopic ellipsometry in the 0.6-6.5 eV of graphene functionalized by: (1) the covalent attachment of hydrogen, nitrogen, oxygen, and fluorine atoms, which strongly affect the optical properties of graphene through a partial sp2-to-sp3 conversion of carbon, (2) the non-covalent interaction with organic molecules such as porphyrins that interact with graphene through π-electrons, and (3) a variety of metals nanoparticles, like Au, Ag, Ga, to create a versatile graphene-based platform for plasmonics in frequency range from the terahertz to the visible.
The graphene is grown by chemical vapor deposition (CVD) and transferred to glass substrates with coverage higher than 98%. This assures large area graphene samples that can easily accommodate the ellipsometric probing light spot avoiding uncontrolled effects due to undefined substrate/graphene boundaries. With the availability of high quality samples, effect of thickness and anisotropy, which have been debated for a while, are clarified.

Data on the real time monitoring of graphene optical properties by spectroscopic ellipsometry that allows for an unprecedented control over the degree of functionalization will also be presented. The perspective of this work is twofold. From the fundamental point of view, in the investigated spectral range, the band structure of graphene has saddles and Hove-singularities at the M points of the Brillouin zone, with possible excitonic effects. Focusing on the analysis of these singularities, many-body effects for all the graphene-derivatives mentioned above are described.

From the technological point of view, it will be shown how the optical measurements can serves to clarify and explain the occurrence and stability of the doping of graphene by the various heteroatoms and molecules, the electron transfer between graphene and metals and molecules, and finally the sensitivity of the-graphene-platform in sensing gases and biomolecules. Spectroscopic ellipsometry data of functionalized graphene are corroborated by Raman spectroscopy, microscopies and electrical characterizations.

Electrochemical reactions on metal electrodes have been in the focus of many scientific studies and Cu is probably the most investigated example. Mainly, the interest on Cu is motivated by questions concerning e.g. the corrosion behavior or the optimization of electro-polishing procedures. Classical electrochemical approaches contain usually a description of the occurring reaction products and concentrations. However, it is evident that a fundamental understanding also requires knowledge about the microscopic occurrence of the metal-electrolyte interface. Desirable is a functional knowledge as it is obtained already for surfaces in UHV. But unfortunately, most of the classical surface sensitive techniques cannot be applied in liquid environments. Thus it is not surprising that many fundamental issues in electrochemical reactions are still unsolved.

In our work we combine reflection anisotropy spectroscopy, spectroscopic ellipsometry, and a homemade electrochemical scanning tunneling microscope to study Cu single crystals in hydrochloric solutions. With these methods we enabled monitoring of the local appearance as well as the dynamics of interface transformations/reactions on the atomic scale. In particular it was possible to explain for the (110) surface in more detail the correlation of Faraday-current and structural transformation. Here, the Cl adsorption minimizes the surface energy by a formation of monoatomic steps parallel to the [001] direction which finally ends in a faceting of the surface. It turns out that characteristic redox peaks in cyclic voltammograms correlate with the stabilization of certain arrangements of these steps. The structures are formed first by Cu dissolution and at higher anodic potentials by rearrangement of Cu atoms in the surface. It is remarkable that the latter process compares nicely with oxide/chloride induced surface transformations which are observed in UHV. The comparison with the UHV results in turn is used to achieve a more comprehensive model for the processes in electrochemical environment.

**Helium Ion Microscopy Focus Topic**

**Room: 316 - Session HI+2D+AS+BI+MC-ThM**

**Fundamental Aspects and Imaging with the Ion Microscope**

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

**8:00am HI+2D+AS+BI+MC-ThM**

**He+ and Ne+ Ion Beam Microscopy and Microanalysis. David C. Joy, University of Tennessee, Oak Ridge National Laboratory**

INVITED

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

The production of X-rays depends on the speed of the incident particle, not on its energy. At typical Everhart–Thornley energies the He+ or Ne+ ions are traveling too slowly to generate X-rays so another approach is required for chemical microanalysis. The most promising option is “Time of Flight–Secondary Ion Mass Spectrometry” (TOF-SIMS). Here the incoming ion “splashes” material from the top few layers of the specimen surface. These fragments are then characterized by determining their mass to charge ratios. The chemical data this generates is much more detailed than the bare list of elements that is produced by X-ray microanalysis.
As Field Ion Sources (GFIIs), there is potential for operation in scanning ion microscopes (SIMs) and our efforts to prepare and characterize SAT ion emission will be discussed. It will be shown that etching to a single atom tip occurs through symmetric structure, and leads to a predictable last atom. SATs can be prepared reproducibly with emission along a fixed direction for all tip rebuilds. It will also be shown that the emission properties of the SAT can be altered by shaping of the tip Shank during the etching procedure. In this manner, the operating voltage can be controlled and a lensing effect of the tip base is demonstrated. During formation, the tip shape can be evaluated by using both helium and neon imaging gases. The stability of helium and neon ion beams generated by SATs will also be demonstrated and compared to other tip orientations. The remarkable robustness of these tips to atmosphere exposure will also be shown and the ability to prepare SATs from material other than tungsten will be demonstrated.

SATs also have utility in electron emission. By shaping the tip appropriately, electron emission characteristics can also be tailored and the coherence properties of the electron beam generated by SATs can be investigated. Recent experiments have demonstrated the use of holographic measurements in a low-energy electron point source microscope. Initial utility in scan probe experiments including atomic force microscopy and scanning tunneling microscopy will also be discussed.


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

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

11:40am HI+2D+AS+BI+MC-ThM12 Helium Ion Microscopy of Biological Cells. Natalie Frese, A. Beyer, M. Schärmann, B. Kalschmidt, C. Kaltenschmidt, A. Götzhäuser, University of Bielefeld, Germany

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

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

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

MILDI mass spectrometry is an emerging tool for detecting changes in brain tissue. An ~20 nm thick region of rat brain tissue implanted with 10^15 cm^-2 Ag(400) nanoparticles (NP) ions at 40 keV, produces analytically useful signals of lipids, peptides and proteins using a pulsed nitrogen laser [1]. When a dose of 10^15 cm^-2 500 eV AgNP (approximately 6 nm diameter) is implanted as a matrix, only lipids are detected [2]. To understand this it is essential to measure the spatial distribution of the nanoparticles. We have used Single Atom Field Backscattering Helium Ion Imaging to determine the Ag NP distributions and areal densities in an implanted coronal rat brain section. We then correlate the ion beam analysis and imaging with individual lipid intensities from several hundred MILDI mass distributions. The results show a high degree of uniformity of the Ag atomic and particulate distribution on a sub-micron scale among different regions of the tissue. Helium Ion Microscopy provides verification of NP matrix uniformity, validating the use of MILDI for quantitative mass analysis. This work is partially supported by NSF (DMR 1126468), NIH (R44DA030853-03) and IAMDN.


Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic

Room: 317 - Session QC+AS+BI+MN-ThM

Fundamentals and Method Development of QCM Moderator: Ralf Richter, CIC biomaGUNE & MPI for Intelligent Systems, W.K. Hiebert, University of Alberta and The National Institute for Nanotechnology

8:40am QC+AS+BI+MN-ThM3 High-Frequency Contact Mechanics Studies with a QCM. Diethelm Johannsmann, Clausthal University of Technology, Germany

INVITED

Studying particulate objects with a QCM is challenging with regard to interpretation, but also of outstanding interest. Potential samples would be
During the past decade, nanoparticles attracted a great deal of attention and plays a key role for the prediction of nanoparticle powder behavior. Hence, a fundamental understanding of the processes and forces involved within a defined layer of SiO₂ nanoparticles was studied by means of a novel in-situ analytical setup allowing for combined quartz crystal microbalance with dissipation analysis (QCM-D) and Fourier transformation infrared reflection spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change (ΔΓ), electron microscopy (TEM) and particle sizes using various types of nanoparticles with diameters ranging from ~5 nm to ~110 nm and compared the results with absolute layer thickness of the particle film; and this quantity, in turn, can be related to the average particle diameter. To validate the approach, we determined particle sizes using various types of nanoparticles with diameters ranging from ~5 nm to ~110 nm and compared the results with electron microscopy (TEM). We found that accurate particle sizing is possible, but requires firm coupling between the particle and quartz crystal microbalance surface. As a side aspect, the flow pattern amounts to a diagnostic for identifying the strength of the nanoparticle-surface interaction. We will also describe our ongoing work where we are studying the QCM-D response to the deposition of macroscopic particles, which contrast to macroscopic particles, nanoparticle flow properties are mainly governed by the particle-surface interactions. The forces determining these interactions strongly vary not only with the material properties but also with surface chemical composition as well as the environmental conditions.

In the presented study,[1] water adsorption and capillary bridge formation within a defined layer of SiO₂ nanoparticles was studied by means of a novel in situ analytical setup allowing for combined quartz crystal microbalance with dissipation analysis (QCM-D) and Fourier transformation infrared reflection spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change (Δm) and changes in the contact mechanics, indicated by dissipation changes (ΔΓ), whereas the other FT-IRRAS allowed the characterisation of the adsorbed water structure. Employing peak deconvolution to the OH- signal in the region of 3400 cm⁻¹, “ice-like” and “liquid-like” water structures could be clearly identified. Combined measurements show that for a monolayer of monodisperse SiO₂ particles with a diameter of about 250 nm the adsorption of water leads to a linear increase in dissipation for relative humidity (RH) values up to 60%. Subsequently, the strong increase in dissipation between 60% and 80% RH was attributed to the actual liquid bridge formation. This result was supported by the predominant growth of “liquid-like” water during the bridge formation phase indicated by the corresponding FT-IR data. Furthermore, for RH > 90% a decrease in dissipation was detected indicating the merging of capillaries and the onset of a water film formation. Overall, our results indicate that combined in-situ QCM-D and FT-IRRAS analysis enables a qualitative and quantitative analysis of water adsorption and capillary bridge formation in particle layers.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic

Room: 315 - Session SM+AS+BI+PS-ThM

Plasma Processing of Antimicrobial Materials and Devices

Moderator: Heather Canavan, University of New Mexico, Morgan Hawker, Colorado State University

8:00am SM+AS+BI+PS-ThM1 Plasma Polymers: Dogma, Characterization and Challenges. Sally McArthur, Swinburne University of Technology, Australia

Plasma polymers, the dogma tells us are densely cross-linked, pinhole free films that adhere to virtually any dry surface. But when you are working at low power and trying to retain specific functional groups within your films, is this still true? How does environment (pH, salt concentration) effect film behaviour and what do responses to change in environment tell us about the nature of these films? This talk will explore methods for studying the physicochemical behaviours of plasma polymer films and discuss how these films can be manipulated address specific biomaterials challenges.

8:40am SM+AS+BI+PS-ThM3 The Role of Plasma Surface Modification in Antimicrobial Thin Films and Strategies. Renate Foerch, FhG-ICT-IMM, Germany

“Delivery on demand” has become a key issue in the development of solutions for bacterial infection and the evolution of resistance. Antimicrobial bioactive coatings may be thin layers, scaffolds or hybrid materials with chemically immobilized or physically embedded antimicrobial substances that act while tethered to a surface or that are released either passively or upon a stimulus. Examples include burst release systems of an antimicrobial from plasma polymerised thin films that have led to recent efforts aiming to develop, characterize and evaluate nanocomposite coatings consisting of thin films, nanoparticles and nanocarrier systems. The nanocomposite coatings are formulated to respond to specific changes in the surrounding environment. The work to be described is part of a European-Australian effort to investigate new strategies to combat microbial infection; it draws expertise from plasma assisted technologies and wet chemical post plasma attachment of responsive nanocounters carrying an antimicrobial to treat bacterial infection.


To direct protein and cellular behavior at the surface of synthetic materials, both localized chemical signaling and control over surface properties are required. To achieve requisite drug delivery dosages, hydrophobic polymers are often employed that slowly elute a therapeutic agent from the bulk material into systemic circulation. However, the surface free energy of the hydrophobic material can lead to deposition of undesired proteins and activation of the clotting. To overcome these challenges, advanced material platforms are needed to achieve localized therapeutic action and customizable surface properties. Herein, we present the development of H2O(v) plasma-treated PLGA-nitric oxide (NO) releasing materials. NO is a well-established anti-platelet and anti-microbial agent, and the NO release rate can be controlled by the hydrophobic nature of the bulk material where it was incorporated. Plasma treatment conditions were optimized to maintaining the NO release function while rendering the surface hydrophilicity. Despite the plasma conditions employed, the material retained 80-90% of the S-nitrosothiol content, while the NO release profiles were unaltered compared to the control. The change in the surface wettability was confirmed by water contact angle measurements. Extensive surface (XPS) and bulk (ATR FT-IR) chemical characterization demonstrated that the changes in wettability was due to the implantation of O-containing surface functional groups such as carbonyl and hydroxyl groups. In addition, optical profilometry analysis confirmed no statistically significant changes in the surface roughness compared to the control. Furthermore, the materials show minimal hydrophobic recovery after several days stored at -20°C. By combining both chemical signaling and surface treatments into one material, we expect to reduce activation of clotting cascade and enhance the biocompatibility of the materials.
Protein Adsortion, Marvin Mecwan, J. Stein, W. Cividino, University of Washington, X. Dong, Eli Lilly and Company, B. Rattier, University of Washington

Proteins irreversibly adsorb onto surface, causing losses from solution, denaturation, as well as aggregation. Hence, there have been recent efforts in the pharmaceutical industry to address the manufacturing, packaging and delivery of protein-based pharmaceuticals. We propose the use of radio-frequency (RF) plasma deposition to create coatings on substrates relevant to the pharmaceutical industry—glass, stainless steel and cyclic olefin polymer (COP). The monomers of choice were acrylic acid (AA) and tetraglyme (TG) (hydrophilic), and perfluoropropylene (C3F6) and perfluoromethyl vinyl ether (C3F6O) (hydrophobic). All monomers were successfully plasma coated on all substrates, and did not delaminate as was determined from survey and detailed ESCA scans. Furthermore, no peaks associated with the substrates were seen in the scans, which indicate that the plasma coating are at least 100Å thick. Protein adsorption studies were carried out using 0.1mg/mL solution of I-125 tagged bovine IgG by adsorbing the tagged protein on the plasma treated substrates for an hour. All hydrophobic monomer plasma treated substrates had lesser protein adsorbed on their surfaces (~2ng/cm²) as compared to hydrophobic plasma treated substrates (10-14 ng/cm²). This is in comparison to untreated controls that had 200-300 ng/cm² protein adsorbed on the surface. Furthermore, following ISO 10993-5 guidelines, by performing cytotoxicity studies using NIH-3T3 fibroblasts all plasma treated substrates were determined to be non-cytotoxic. Hence, these results indicate that radio-frequency plasma treatment could lead to a new generation of surfaces that will be particularly effective for protein manufacture, storage and delivery. Future studies will be aimed at determining plasma coating thickness, protein aggregation assessment as well as studying the bonding strength of the proteins to the plasma treated surfaces.


Artificial porous polymeric membranes are used in many applications including water filtration systems and devices to treat blood for a broad variety of therapeutic purposes. In water filtration systems, membranes are used to remove colloidal particles and organic molecules from the watercourse and, in medical treatments, they function primarily to eliminate toxins from the blood before it is returned to the patient’s body. Although these are very different applications, both are affected by membrane fouling from proteins, toxins, bacteria, and cells, which significantly decrease flow through the porous material. Surface modification techniques that retain the desired bulk properties are the ideal method for obtaining low-fouling membranes, thus extending their life-time in applications where they are exposed to fouling conditions. Here, we will present the properties of polysulfone ultrafiltration membranes subjected to H2O plasma and their performance when exposed to proteins and bacteria. Plasma treated membranes showed enhanced hydrodynamic characteristics (i.e. increase in water flux) as a result of their high hydrophilicity. Notably, hydrophilic characteristics were retained for more than six months, ensuring top-shelf stability of the surface treatment. In terms of protein fouling performance, treated membranes show less bovine serum albumin adsorption than untreated membranes and cleaning of treated fouled membranes yields 70-90% flux recovery depending on plasma treatment time. This surface modification provides a mechanism for extending the life-time of the membranes.

Membrane Science: The Fundamentals of Charge Transport at Oxide and Ferroelectric Interfaces, Ramsey Kraya, L. Y. Kraya, University of Pennsylvania

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

Epitaxial Graphene on Nanostructured Silicon Carbide, Phillip First, Georgia Institute of Technology

Graphene grown epitaxially on silicon carbide conforms to nanofaceted step edges, even for step heights of many nanometers. The “sidewall” nanoribbons that result show astounding transport characteristics (~15 um ballistic length at room temperature), as demonstrated by others, but the physical basis for these results is still not certain. In our STM measurements of sidewall nanoribbons, we find an extended 1D region with electronic structure much different than 2D graphene. Spectroscopic results on graphene near nanofacets indicate a strain gradient and a rapid change in the doping. Such strong gradients may be key to understanding the ballistic transport in this system.
9:20am  SP+2D+AS+EM+MC+NS+SS-ThM5  Conductivity of Si(111) - 7 × 7: The Role of a Single Atomic Step. B. Martins, University of Alberta and The National Institute for Nanotechnology, Canada. M. Smeu, H. Guo, McGill University, Canada, Robert Wolok, University of Alberta and The National Institute for Nanotechnology, Canada

The Si(111) - 7 × 7 surface is one of the most interesting semiconductor surfaces because of its complex reconstruction and fascinating electronic properties. While it is known that the Si - 7 × 7 is a conducting surface, the exact surface conductivity has eluded consensus for decades as measured values differ by 7 orders of magnitude. Here we report a combined STM and transport measurement experiment and theory on both the sign and the magnitude of the boundary. The Friedel gaps are different on the monolayer and bilayer sides, which can shift under bias and lead to asymmetric transport upon bias polarity reversal at individual monolayer-bilayer (ML-BL) boundaries. A quantitative agreement is seen between the STM tips on those pads and thereby establish the contacts on this material without any subsequent lithography process, avoiding contaminations introduced by other technological steps. An electron hopping process in localized charge trapping states appears to dominate the transport behavior. We performed temperature-dependent measurements in the range of 82 K to 315 K which demonstrate a variable range hopping (VRH) transport with a very low mobility. Furthermore, the effects of electronic irradiation are examined by exposing the film to electron beam in the SEM in an ultra-high vacuum environment. We found that the irradiation process affect the mobility and also the carrier concentration of the material, with conductance showing a peculiar time-depending relaxation behavior. It is suggested that the presence of defects such as vacancies and antisites create charge trapping states, leading to the low mobility. This is consistent with recent density functional theory calculations where these defects are shown to create localized gap states that can act as scattering centers and thereby reduce the mobility.


The quest for novel two-dimensional (2D) materials has led to the discovery of hybrid heterostructures of graphene and other 2D atomic films [1]. These hybrid heterostructures provide us fascinating playground for exploring electronic and transport properties in 2D materials. Even in graphene itself, there usually exist large amount of extended topological defects, such as grain boundaries, changes in layer thickness, and substrate steps, which divide graphene into grains and domains. These interfaces and boundaries can break the lattice symmetry and are believed to have a significant impact on the electronic properties, especially the transport, in 2D materials. Here, we present our recent study on an asymmetric electron transport upon bias polarity reversal at individual monolayer-bilayer (ML-BL) boundaries in epitaxial graphene on SiC (0001), revealed by multi-probe scanning tunneling microscopy [2,3]. A greater voltage drop is observed when the current flows from monolayer to bilayer graphene than in the reverse direction, and the difference remains nearly unchanged when bias exceeds a threshold of ~ 60mV. A nontrivial temperature dependency of the boundary due to the thermopower difference between the two sides, which however is too small to account for the observed asymmetry. Interestingly, this asymmetry is not from a typical nonlinear conductance due to electron transmission through an asymmetric potential. Rather, it indicates the opening of an energy gap at the Fermi energy. Our theoretical analysis finds that Friedel charge oscillation opens a gap for electrons with wave vectors perpendicular to the boundary. The Friedel gaps are different on the monolayer and bilayer sides, which can shift under bias and lead to asymmetric transport upon reversing the bias polarity. A quantitative agreement is seen between experiment and theory on both the sign and the magnitude of the asymmetry.


11:00am  SP+2D+AS+EM+MC+NS+SS-ThM10  Defect-mediated Transport in CVD-grown Monolayer MoS2. Corentin Durand, J. Fowlkes, Oak Ridge National Laboratory. S. Najmaei, J. Liu, Rice University, A.P. Li, Oak Ridge National Laboratory

Transition metal dichalcogenides like molybdenum disulphide (MoS2) have attracted great interest as candidate to fill the need of 2 dimensional semiconductor materials. By controlling the thickness, the bandgap of MoS2 thin films can be tuned from 1.2 eV (bulk material, indirect bandgap) to 1.8 eV (monolayer film, direct bandgap). Recently, researchers succeeded in growing monolayered MoS2 by chemical vapor deposition (CVD) on silicon dioxide (SiO2) substrate, showing the possibility of low cost scalable device fabrication. However, the mobility reported on exfoliated MoS2 monolayers exceeds 200 cm/V.s’, whereas the measurements realized on CVD growth MoS2 monolayers reveal a mobility value that is usually 1-2 orders of magnitude lower. Here, we study the transport properties of CVD-grown monolayer on SiO2/Si substrate. We directly measure the resistivity and the mobility of the material with a field-effect transistor architecture by using a cryogenic four-probe scanning tunneling microscope (STM), the Si substrate being used as back-gate. In order to ensure reliable electrical contacts, we fabricate platinum pads (4x4 µm2) on individual MoS2 crystal contacts, we fabricate platinum pads (4x4 µm2) on individual MoS2 crystal domains by using an electron-beam induced deposition technique. The combination of the STM scanners and a scanning electron microscope (SEM) enables us to connect the STM tips on those pads and thereby establish the contacts on this material without any subsequent lithography process, avoiding contaminations introduced by other technological steps. An electron hopping process in localized charge trapping states appears to dominate the transport behavior. We performed temperature-dependent measurements in the range of 82 K to 315 K which demonstrate a variable range hopping (VRH) transport with a very low mobility. Furthermore, the effects of electronic irradiation are examined by exposing the film to electron beam in the SEM in an ultra-high vacuum environment. We found that the irradiation process affect the mobility and also the carrier concentration of the material, with conductance showing a peculiar time-depending relaxation behavior. It is suggested that the presence of defects such as vacancies and antisites create charge trapping states, leading to the low mobility. This is consistent with recent density functional theory calculations where these defects are shown to create localized gap states that can act as scattering centers and thereby reduce the mobility.
this context new types of spin order were proposed, e.g. for Au/Si(553) [3]
and found to be consistent with experiment. As a further example, the
Pb/Si(557) system close to monolayer coverage turned out to be an
intriguing model system that demonstrates the wealth of phenomena to be
expected in quasi-1D physics. Adsorbate induced electronic stabilization
leads to (223) refacetting of the (557) surface, to opening of a band gap, to
Fermi nesting normal to the steps [4], and to the formation of a charge
density wave. Rashba splitting is so large that it causes in-plane anti-
ferromagnetic spin polarization along the steps with twice the step
periodicity resulting in a combined spin-charge density wave. New
superstructures are formed by an excess Pb coverage up to 0.1ML due to
ordered step decoration indicating strong electron-electron correlation
across steps. This leads to new long range ordered states and formation of a
sequence of 1D charge density waves up to a concentration of 1.5 ML, but
also, as very recent angular and spin resolved photoemission studies show,
to new ordered spin states.

Mineral carbon sequestration is one of the important means to store CO₂ in Qafoku, A. Felmy
and Kruse, T. Visart de Bocarmé.

In this presentation we describe the design and examples of applications of the use of an environmental cell integrated into a LEAP atom probe. The use of such a cell helps to open up the field of in-situ gas-solid reactions by permitting one to study surface and near surface reactions which are closer to ambient conditions than is possible in traditional surfaces science studies. The implications for this experimental approach in the context of the study of catalysts and nanomaterials are discussed.

In the catalytic hydrogenation of NO₂ over platinum field emitter tips has been investigated by means of field emission techniques (FEM), as well as field ion microscopy (FIM), to be an efficient method to study the dynamics of catalytic reactions occurring at the surface of a nanosized metal tip, which represents a good model of a single catalytic nanoparticle. These studies are performed during the ongoing reaction which is imaged in real time and space. Nanoscale resolution allows for a local indication of the instantaneous surface composition.

The microscope is run as an open nanoreactor, ensuring that the system is kept far from thermodynamic equilibrium. Under these conditions, chemical reactions can induce time and space symmetry breaking of the composition of a system, for which periodic oscillations and target patterns are well-known examples.

Self-sustained periodic oscillations have been reported for the NO₂ reduction. By increasing the time resolution of the system, it is now possible to study the emergence of these oscillations and to observe the propagation of chemical waves at the nanoscale, on a single facet of a nanocrystal. The velocity of wave propagation is estimated to be in the μm/s range, which is in accordance with previous studies of catalytic reaction at the mesoscale.

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

In the case of inhomogeneous materials the permittivity additionally becomes k-dependent ε(ω, k); it exhibits spatial dispersion. For most artificial nanostructures, dubbed metamaterials, the building blocks are in the range 1/10 < P < 1/2. During the last couple of years it has become clear that in general it is not possible for these kinds of materials to define effective optical parameters, which are independent of the angle of incidence of the probing light. There optical response is intrinsically k-dependent.

With Mueller-matrix spectroscopic ellipsometry the entire optical response of artificial nanostructures can be characterized. For this the Mueller-matrix elements m(θ, α, ω), which depends on the angle of incidence q, the azimuth orientation a and the energy, had to be measured over the complete angular and a wide frequency range. Visualizing the results in polar contour
Generalized Ellipsometry on Sculptured Thin Films with Forward gratings by fully exploiting the rich information hidden in the measured also can be applied to accurately characterize asymmetric nanoimprinted the direction of profile asymmetry. In contrast, MME not only has good asymmetric grating structure due to the lack of capability of distinguishing (3) Conventional ellipsometric scatterometry has difficulties measuring structures, can be only handled by MME.

(2) Not only further improvement in the measurement accuracy and fitting achieved by performing MME measurements in the optimal configuration. and residual layer thickne ss of nanoimprinted grating structures can be

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

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

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

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

3:20pm EL+AS+EM+MC+SS-ThA4 Vector Magneto-Optical Generalized Ellipsometry on Sculptured Thin Films with Forward Calculated Uniaxial Response Simulation. Chad Briley, T. Hofmann, University of Nebraska-Lincoln, D. Schmidt, National University of Singapore, E. Schubert, M. Schubert, University of Nebraska-Lincoln. We present the vector magneto-optical generalized ellipsometric (VMOGE) response and forward calculated simulations of ferromagnetic slanted columnar thin films. Directional hysteresis magnetization scans were performed with an octu-pole vector magnet at room temperature on slanted columnar thin films samples of permalloy grown by glancing angle deposition by an atomic layer deposited Al2O3 as topcoat. Model analyses of the measured Mueller matrix ellipsometric data through a point-by-point best match model process determines the magneto-optical (MO) dielectric tensor. Three dimensional rendering of the anti-symmetric off-diagonal elements of the MO dielectric tensor reveal a uniaxial magnetic response of the thin film along the long axis of the column. The magnetic response was subsequently modeled by a best match model process with uniaxial hysteretic response governed by the shape induced anisotropy from the physical geometry and orientation of the nano-columns. By using model parameters for normalized saturation [Ms]=1, coercivity [Hc]=50 mT, and remanence [Mr]=0.99999 [Ms] the forward calculated magnetic simulations described the observed magneto-optical response for all measured orientations of the nano-columns with respect to all magnetizing field directions generated by the vector magnet.


4:00pm EL+AS+EM+MC+SS-ThA6 In Situ Generalized Ellipsometry Characterization of Silicon Nanostructures during Lithium-ion Intercalation. Derek Sekora, R.Y. Lai, T. Hofmann, M. Schubert, E. Schubert, University of Nebraska-Lincoln. Nanostructured silicon has emerged as a leading candidate for improved lithium-ion battery electrode design. The combined highly accessible surface area and nanoscale spacing for volumetric lattice expansion of nanostructured thin films have shown improved cycle lifetime over bulk-like silicon films. Additionally, ultra-thin passivation layers have been reported to increase the longevity and stability of silicon thin film electrodes. Very little in-situ information has been reported on silicon films during the complicated lithiation process. Furthermore, what information available has been limited to the study of bulk-like the thin film. The advantageous geometry of glancing angle deposited (GLAD) thin films allows for the strain from lithiation to affect individual nanostructures in comparison to the bulk response. For this reason, alumina passivated GLAD silicon films were grown for use as working electrodes in half cell electrochemical experiments.

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

4:20pm EL+AS+EM+MC+SS-ThA7 Characterization of SiO2 Nanoparticle Layers on a Glass Substrate by Spectroscopic Imaging Ellipsometry and AFM. Peter H. Thiessen, Accurion GmbH, Germany. G. Hearn, Accurion Inc., C. Röling, Accurion GmbH, Germany. The well-directed organization of nanoparticles is of increasing technical and scientific interest. One approach is the organization of nanoparticles at the air/water interface for applications, like producing 2D colloidal crystals or nanowires. For example, Gil et al. (2007) monitored the formation of 2D colloidal crystals by Langmuir–Blodgett technique. They used Brewster angle microscopy to observe the film quality. Zang et al. (2009) have also studied silica nanoparticle layers at the air/water interface by multiple angle of incidence ellipsometry. For data interpretation, a two-layer model was introduced. With this model, the radius of interfacial aggregates and the contact angle of the nanoparticle surface at the air/water interface were obtained.

In this paper different line shaped pattern of SiO2 nanoparticles were characterized by spectroscopic imaging ellipsometry in the wavelength range between 360 and 1000 nm and by AFM. The samples were provided by the research group of Professor Y. Mori, Doshisha University, Japan. The work shows the unique capability of imaging ellipsometry in characterizing patterned surfaces. We started with a pre inspection of the surface by imaging ellipsometric contrast microscopy. Tiny regions of interest (ROIs) were placed on interesting areas like on different steps of the stripes and Delta and Psi spectra were recorded. The next step in characterization was the mapping of Delta and Psi with pixel resolution of the detector. The same samples were also characterized with an AFM. The results optical modelling are in good agreement with the results of the scanning method.


5:00pm EL+AS+EM+MC+SS-ThA9 Dielectric Tensor Model for Inter Landau-level Transitions in Highly Oriented Pyrolytic Graphite and Epitaxial Graphene – Symmetry Properties, Energy Conservation and Plasma Coupling. Philipp Kühne, Linköping University, Sweden. The report on polarization sensitive, magneto-optic, reflection-type Landau level (LL) spectroscopy at low temperatures by using the integrated optical
Hall effect instrument in the mid-infrared spectral range (600 – 4000 cm⁻¹) on highly oriented pyrolytic graphite (HOPG) and epitaxial graphene grown on C-face silicon carbide by thermal decomposition. In both sample systems we observe a multitude of inter-LL transitions. Inter-LL transitions in HOPG possess polarization mode mixing polarization selection rules characteristics, while polarization mode conserving and polarization mode mixing inter-LL transitions are observed in epitaxial graphite which can be assigned to single- and Bernal stacked (ABA) multi-layer graphene, respectively. We present a new dielectric tensor model for inter-LL transitions which explains all experimentally observed line-shapes. For inter-LL transitions in multi-layer graphene and HOPG we employ this new model together with energy conservation considerations, to show that these polarization mode mixing inter-LL transitions couple with a free charge carrier plasma. Finally, inter-LL transition energy parameters are determined and discussed. ¹ P. Kühne, et. al., Rev. Sci. Instrum., accepted (2014) ² P. Kühne, et al., Phys. Rev. Lett. 111, 077402 (2013)
 Meanwhile interact with the target atoms. The low backscattering of the He+ EUV photons. Both primary particle beams traverse the resist and resist.

In this paper we show 30 keV He+ ions exposures of contact holes and lines etch) nanomachining and IBID properties and electrical invasiveness that relaxes by the excitation of Secondary Electrons (SEs). A collision of a 20-30 keV helium ion with a target atom directly releases low-energy SEs. Each ion scatters several times in the resist layer, thus enabling resist etching. As a result FIB nanomachining capabilities have been steadily eroding over the last several generations, limiting the types of circuit modifications that can be successfully completed. There are however, several promising new ion beam scaling R&D initiatives that provide hope of enabling further nanomachining scaling into the sub 10nm process node.

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

References


For the introduction of EUV lithography, development of high performance EUV resist is of key importance. This development involves studies into sensitivity, resolving power and pattern uniformity. We have used a sub-nanometer-sized 30 keV helium ion beam to expose chemically amplified (CAR) EUV resists. There are remarkable similarities in the response of resists to He+ ions and EUV photons. Both primary particle beams traverse the resist and meanwhile interact with the target atoms. The low backscattering of the He+ ions results in ultra-low proximity effects, which is similar to EUV exposure s. Absorption of an EUV photon creates a high-energy electron that relaxes by the excitation of Secondary Electrons (SEs). A collision of a 20-30 keV helium ion with a target atom directly releases low-energy SEs. Each ion scatters several times in the resist layer, thus enabling resist exposure at very low doses per CH. The energy spectra of SEs generated by EUV and He+ are remarkably alike. These SEs, in turn, activate the resist.

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


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

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

Here, the latest results from an experimental investigation into the HIBL technique will be presented. Areas of PMMA films of various thicknesses are exposed to different helium ion doses. After subsequent development in MIBK/IPA, atomic force microscopy is used to measure residual layer thickness in order to generate exposure response curves for different initial thicknesses of resist. High sensitivity is confirmed with full exposure of 50 nm thick layers achieved with a helium ion dose of only ~2 µC/cm2. Experiments to characterise minimum feature size and proximity effects are currently underway. The use of other high resolution resists will also be investigated with the aim of providing a thorough assessment of the capabilities and limitations of this emerging nano-patterning technique.


Sub-100nm Nanofabrication using Helium and Neon Ion Beams. J. Sagar1, C. R. Nash1, N. Braz1,2, T. Wootton1,2, M. J. L. Sourbies1,2, T.-T. Nguyen1, R. B. Jackman1, and P. A. Warburton1

1London Centre for Nanotechnology, University College London, 17-19 Gordon Street, London, WCH1 0AH, UK
2Department of Electrical and Electronic Engineering, University College London, London, WC1E 7JE, UK.

Using a Zeiss Orion NanoFab we have created sub-100nm devices for experiments in quantum electronics and nanophotonics. The Orion NanoFab has been able to form an ion beam with a very large area mill of conventional liquid Ga FIB but with considerably enhanced fidelity due to a large probe size (≤ 5nm). Using a Ne ion beam we have fabricated two kinds of nanoscale superconducting devices: a superconducting nanowire based on a compound low-Tc superconductor; and an array of nanoscale Josephson junctions based on a compound oxide high-Tc superconductor. The use of an inert-gas ion species in these devices is extremely important as Ga implantation into superconducting materials has previously been shown to suppress superconductivity. The extremely small probe size of the He GFIS has allowed us to create sub-20nm apertures in a variety of materials. Sub-20nm apertures in InAs nanowires and in graphene have been fabricated for experiments in quantum coherent electronics and quantum nanophotonics respectively.

Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic

Room: 317 - Session QC+AS+BI+MN-ThA

Applications of QCM

Moderator: Electra Gizeli, IMBB-FORTH, Heraklion, Crete, Greece, Adam Osslo, McGill University, Canada.

2:20pm QC+AS+BI+MN-ThA1 Permeability of a Model Stratum Corneum Lipid Membrane, Daeyeon Lee, University of Pennsylvania

INVITED

The stratum corneum (SC), composed of corneocytes and intercellular lipid membranes, is the outermost layer of the epidermis, and its main function is the regulation of water loss from the skin. The major components of the SC lipid membranes are ceramides (CER), cholesterol (CHOL), and free fatty acids (FFA), which are organized in multilamellar structures between corneocytes. The intercellular SC lipid membrane is believed to provide the
main pathway for the transport of water and other substances through the skin. While changes in the composition of the SC lipid membranes due to intrinsic and/or extrinsic factors have been shown to affect the organization of the lipid molecules, little is known about the effect of compositional changes on their water permeability. In this talk, I will present our results on the effect of composition on the permeability of a model SC lipid membrane consisting of ceramide, palmitic acid, and cholesterol using a quartz crystal microbalance with dissipation monitoring (QCM-D). The QCM-D method enables the direct determination of the diffusivity (D), solubility (S), and permeability (P) of water through the model SC lipid membranes. In the first part, I will discuss the effect of membrane composition on the water permeability of the model SC lipid membrane. We find that D and S weakly depend on the chain length of saturated fatty acids, while P shows no significant dependence. In contrast, the saturation level of fatty acids and the structure of ceramide have a significant influence on D and S, respectively, resulting in significant changes in P. In the second part of the talk, I will present our recent work on the effect of common anionic surfactants on the water permeability of the model SC lipid membrane. Particularly, the effect of sodium dodecyl sulfate (SDS) and sodium lauryl ether sulfate (SLES) with one or three ethoxy groups on the water permeability of the model SC lipid membrane is compared.

3:00pm QC+AS+BI+MN-ThA3 Investigation of Interaction between a Monoclonal Antibody and Solid Surfaces via Multiple Surface Analytical Techniques. X. Dong, C.A.J. Kemp, Z. Xiao, E. Lilly and Company

The interaction between proteins and surfaces is an important topic in the field of biomaterials. With the development of monoclonal antibody products, there is increasing interest in understanding the nature of the interactions between antibodies and the solid surfaces they contact during manufacturing processes and storage. In this study, a monoclonal antibody was introduced to quartz crystal microbalance (QCM) substrates coated with gold, stainless steel and silicon carbide. The samples were characterized by multiple surface analytical techniques, including TOF-SIMS and XPS. The preliminary XPS results suggest that the protein adsorbed onto higher concentrations of stainless steel and silicon carbide, while nitrogen concentration detected on stainless steel is slightly higher than on silicon carbide. This is generally consistent with the QCM results. TOF-SIMS spectra also suggest that the interaction between the antibody and three substrates is not the same. The fragmentation patterns detected in the TOF-SIMS spectra obtained from silicon carbide and stainless steel are similar to each other, but they are different from those detected on gold. The interaction between the antibody and stainless steel surfaces will be further studied to understand the influence of surface morphology.


Angle, M. Biophysical Chemistry, Germany, Ralf Richter, CIC biomaGUNE & Université Grenoble Alpes & MPI Intelligent Systems, Spain

Nature has evolved hydrogel-like materials that are exquisitely designed to perform specific biological functions. An example of such a material is the nuclear pore permeability barrier, a nano-sized meshwork of intrinsically defined biomimetic film affords detailed and quantitative characterization – useful towards the design of bioinspired species-selective filtering devices. In this study, we examined the deposition of NPs onto surface-immobilized proteins to determine the importance of protein-rich domains in the interfacial interactions between NPs and biofilms. Such interfacial processes are the initial and potentially rate-limiting step in NP-biofilm interactions. The deposition kinetics and extent of model hematite (α-Fe2O3) NPs on glass or quartz-coated silica surfaces were quantitated by quartz crystal microbalance with dissipation monitoring (QCM-D). Model proteins including bovine serum albumin (BSA) and lysozyme as well as bacterial total proteins were used herein. The proteins were initially adsorbed onto either negatively-charged bare or positively-charged poly-L-lysine (PLL)-precoated silica sensors to assess the effects of the orientation of surface-immobilized proteins. In addition to QCM-D, other complementary surface-sensitive techniques such as XPS, ARXPS, and TOF-SIMS were used to characterize the interactions between the NPs and the protein-coated surfaces.

QCM-D results indicate that for all tested proteins, the total deposition extent of hematite NPs was significantly greater on protein layers that were adsorbed onto bare silica compared to PLL-precoated silica sensors. TOF-SIMS results showed that the amino acid profiles of the topmost surface of the protein layers on bare and PLL-precoated silica sensors were distinctly different, suggesting that NP deposition was greatly influenced by the orientation of the surface-immobilized proteins. Both the extents and rates of NP deposition were also dependent on the type of model protein. Based on the surface charge, topography, and hydrophobicity characterization results, the observed interfacial interactions between hematite NPs and surface-immobilized proteins appeared not to be controlled by one dominant interaction force but by a combination of electrostatic, steric, hydrophobic, and other interactions.

4:20pm QC+AS+BI+MN-ThA7 Association and Entrainment of Membrane-Targeted Nanoparticles with Different Binding Avidity: A QCM-D and Single Particle Tracking Study. Anders Lundgren*, B. Aagnarsson, S. Block, F. Höök, Chalmers University of Technology, Sweden

Nanoparticles specifically targeted to receptors in the cell membrane are increasingly used for various applications such as intracellular delivery and visualization of diffusing membrane proteins, so-called single particle tracking. These diverse applications require particles optimized to display different binding properties: In this model study we investigated the effect of particle size and ligand density on the association rate and mobility/entrainment of biotin functionalized core-shell nanoparticles to biotin-conjugated lipids such as anti-carcinoembryonic antigen (anti-CEA) and Gold-PF-PEG. Core-shell nanoparticles were synthesized with two different core sizes, 20 and 50 nm in diameter, and a shell (10 nm) of mixed uncharged, negatively charged and biotinylated PEG-ligands, the biotin content varied from one to several hundreds per particle. Particle binding was examined on the ensemble level using QCM-D and on single particle level using novel light scattering microscopy that will be detailed. At physiological salt conditions, binding of 50 nm particles were weakly dependent on the number of

* QCM Focus Topic Young Investigator Award
displayed biotin ligands, whereas the association of 20 nm particles were strongly attenuated in direct relation to the ligand density. At low salt conditions, binding of the larger particles resembled that of the smaller particles, with a strong dependence on ligand density. PEGylated particles without biotin-ligands did not bind at any condition. Thus, it was concluded that specific particle affinity is strongly attenuated by particle size and surface charge due to different interaction potential between the particle and the surface. On the contrary, no dependence on particle size was observed for fractal mobility. Particles displaying diffusion constants close to 0.4 or 0.8 µm/s irrespective of particle size, was similar to ensemble measurements using FRAP data on FITC-labelled streptavidin (0.5 µm/s). Only particles with a single surface tether show continuous diffusion; after formation of a second surface bond particles got quickly entrapped and formed additional bonds. In QCM-D measurements, this was manifested by a continuously increasing number of bound particles with fractal mobility of the particles, whereas for intermediate ligand densities the diffusion and dynamics of the particles themselves facilitate the formation of additional surface bonds and eventually wrapping.

4:40pm QC+AS+B1+MN-ThA8 Complementary Chemiresistor and QCM Studies of Biomacromolecules as Sorptive Materials for Vapor Sensing, Kan Fu, X. Jiang, B.G. Willis, University of Connecticut

Biomolecules are integral components of current sensing and diagnostic technologies including enzymatic glucose sensors, DNA microarrays, and antigen-antibody assays. The use of biomolecules in non-biological situations, however, may open new windows that may break new boundaries of biomolecule applications in exclusively biological context. Extensive studies have already been performed in biocatalysis using small biomolecules and biomacromolecules, revealing promising results regarding charge transport and conformation dependence. In the area of sorptive chemical sensors, biomacromolecules have inherent advantages over conventional synthetic polymers. DNA oligomers have precisely defined sequences through synthesis, they are monodisperse, and they can self-assemble into nanoscale structures. These features make them interesting for vapor sensing of small molecules.

In this work, a series of 8 custom-designed, single-strand DNA (ssDNA) were integrated with chemiresisitors and QCM to make sensors. Chemiresistor sensors were made by depositing gold nanoparticles functionalized with ssDNA molecules onto microfabricated electrodes, and QCM sensors were made by depositing films of ssDNA on quartz crystals. While chemiresistors give high signal-to-noise ratios and significantly better limits of detection (LODs) and may eventually be the transducer for practical applications, QCM is a purely mass-sensitive technique that reveals fundamental absorption properties in terms of partition coefficients. By exposing these sensors to a series of organic vapors, the resistance change and mass change of the two sensor platforms can be compared. It is demonstrated that similar to previous comparative studies, the ssDNA nanoparticles functionalized with small organic thiols and synthetic polymer modified QCM crystals, the nanoparticle-based chemiresistor response follows the QCM-traced mass change. The studies show that sorption and conductance modulation mechanisms of vapors on biomolecules are similar to sensors with small organic molecules, but the polarity preference is very different. A model relating partition coefficients K in and chemiresistor responses AR/R is thereafter suggested to account for the links between these 2 sensing systems. It needs to be noted that points which deviate from the modeled trends are likely the result of more complex vapor-material interactions. From here, we demonstrate that DNA oligomers are rich in diversity, which may qualify these materials for array-based and specific sensing applications. It also establishes QCM as a useful complementary tool for evaluating materials for various sensing systems.

5:00pm QC+AS+B1+MN-ThA9 The Evolution of Complex Artificial Cell Membranes: Combining Patterned Plasma Polymers and Supported Lipid Bilayers, Hannah Askew, S.L. McArthur, Swinburne University of Technology, Australia

Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. Such models have been useful for studying a variety of processes including cell signalling and drug-membrane interactions. Unfortunately, current models are lacking in their ability to mimic complex micro and nanoscale architectures found within native cell membranes. Many methods of SLB patterning have emerged to form these complex structures. In particular pre-patterned substrates combined with vesicle collapse are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymerisation provides a versatile, one step, dry method of creating thin films of different chemistries on almost any substrate. Successful bilayer formation on such coatings would be beneficial for promoting specific organisation in complex SLB systems using patterned surface chemistries. In the initial stages of this work we studied the effect of plasma polymer chemistry on the lipid structures formed using vesicle collapse. DOPC lipid vesicles were introduced to commonly used coatings formed from plasma polymerised allylamine (ppAAm) and acrylic acid (ppAAc). The coatings were characterised using X-Ray Photoelectron Spectroscopy (XPS), contact angle and Quartz Crystal Microbalance with Dissipation (QCM-D) techniques. Lipid interaction kinetics and lipid mobility were characterised using QCM-D and Fluorescence Recovery after Photobleaching (FRAP) respectively. It was shown that a variety of lipid structures including mobile bilayer can be formed on ppAAm using pH alone to control electrostatic interactions. ppAAm formed immobile vesicular layers under all conditions tested and could therefore be used as a barrier to confine fluid areas of bilayer. Work is now being undertaken to create single and dual plasma polymer patterns on both glass and silicon wafer. Standard photolithography and ion beam methods will be employed to pattern on both a micro and nanoscale. In this way plasma polymer patterns may enable the formation of increasingly complex SLB architectures.

5:20pm QC+AS+B1+MN-ThA10 Applications of QCM in Industrial R&D, Andrej Soukouhak, The Dow Chemical Company

An overview of diverse applications of QCM enabled by its unparalleled sensitivity to mass and viscoelastic properties of thin samples in R&D of The Dow Chemical Company will be presented.

Surface Modification of Materials by Plasmas for Medical Purposes Focus Topic
Room: 315 - Session SM+AS+B1+PS-ThA

Plasma Processing of Biomimetic Materials
Moderator: Sally McArthur, Swinburne University of Technology, Adoracion Pegalajar-Jurado, Colorado State University

2:20pm SM+AS+B1+PS-ThA1 The Chemistry of Plasma Modified 3D Biomaterials, Eloisa Sardella, CNR-IMIP, Italy

INVITED Plasma processing has become a most powerful and versatile tool for surface functionalization of porous materials in biomedical field. Non-equilibrium plasmas have many advantages over wet chemistry approaches: they are highly eco-friendly, have high potentials in developing surfaces with peculiar characteristics, are capable to be part of in-line material processing and most importantly, can be applied to any material. Consequently, it has opened many new opportunities for investigation of surface modification in various fields like tissue and organ regeneration and biosensing. In this talk, we shall give a brief review on the recent developments of plasma processing of porous materials. We shall describe our experience on non-equilibrium plasmas to modify materials of biomedical interest like: scaffolds for tissue engineering and 3D carbon nanotubes carpets for bio-sensing. This research is aimed to gain new insights on the potentialities of plasma processing of biomedical materials. This work is encouraged by a deep characterization of material’s surface and investigation of the material/ bio-environment interface.

3:00pm SM+AS+B1+PS-ThA3 Advantages of Plasma Polymerized Surfaces for Cell Sheet Engineering over Other Deposition Techniques, Bluestein, Canavan, Cooperstein, University of New Mexico, B. Bluestein, University of Washington, J.A. Reed, University of New Mexico

INVITED Poly(N-isopropyl acrylamide) (pNIPAM) undergoes a conformation change in a physiologically relevant temperature range: it is relatively hydrophobic above its lower critical solution temperature (LCST, ~32°C), and mammalian cells are easily cultured on pNIPAM-grafted surfaces. When the temperature is lowered below the LCST, the polymer’s chains rapidly hydrate, and cells detach as intact sheets capable of being used to engineer tissues (“cell sheet engineering”). This behavior has led to a great deal of interest from the bioengineering community, resulting in a variety of film deposition methods, substrate storage techniques, and cell release methods. Unfortunately, this has also resulted in widely varying responses (e.g., % of cells released, biocompatibility and stability of surfaces, etc.) from the resulting cell sheets. In this work, we present a comprehensive comparison of the surface chemistry, biocompatibility, and effect on reversible cell adhesion that results from pNIPAM substrates fabricated using the most common polymerization (free radical and plasma polymerization) and deposition (spin coating and plasma polymerization) techniques. The
relative biocompatibility of different mammalian cells (e.g., endothelial, epithelial, smooth muscle, and fibroblasts) was evaluated using appropriate cytotoxicity tests (MTS, Live/Dead, plating efficiency). The pNIPAM-coated surfaces were evaluated for their thermoresponsiveness and surface chemistry using X-ray photoelectron spectroscopy and goniometry. We find that plasma polymerized NIPAM substrates (pNIPAM) are more stable under a variety of storage conditions prior to their use. Furthermore, when used for cell culture, pNIPAM films exhibit no cytotoxicity toward any of the cell types tested and yield excellent cell detachment (~85%), which is an important consideration for their ultimate use in engineered tissues.

4:00pm SM+AS+B+PS-ThA6 Biofunctionalization of Surfaces by Energetic Ion Implantation: Fundamentals and Recent Progress on Applications, Marcela Bilek, A. Konudyin, E. Kosobroda, G. Yeo, University of Sydney, Australia, S. Wise, Heart Research Institute, Australia, N.J. Worsoby, C.G. dos Remedios, I.S. Weiss, D.R. McKenzie, University of Sydney, Australia

Despite major research efforts in the field of biomaterials, rejection, severe immune responses, scar tissue and poor integration continue to seriously limit the performance of today’s implantable biomedical devices. Implantable biomaterials that interact with their host via an interfacial layer of active biomolecules to direct a desired cellular response to the implant would represent a major leap forward. Another, perhaps equally revolutionary, development that is on the biomedical horizon is the introduction of cost-effective microarrays for fast, highly multiplexed screening for biomarkers on cell membranes and in a variety of analyte solutions.

Both of these advances will rely on the availability of methods to strongly attach biomolecules to surfaces whilst retaining their biological activity. Radicals embedded in nanoscale carbon rich surface layers by energetic ion bombardment can covalently immobilize bioactive proteins [Proc. Nat. Acad. Sci. 108(35) pp.14405-14410 (2011)] onto the surfaces of a wide range of materials, including polymers, metals, semiconductors and ceramics . This new approach delivers the strength and stability of covalent coupling without the need for chemical linker molecules and multi-step wet chemistry. Immobilization occurs in a single step directly from solution and the hydrophilic nature of the surface ensures that the bioactive 3D shapes of the protein molecules are minimally disturbed.

This presentation will describe recently developed approaches that use energetic ions extracted from plasma to facilitate simple, one-step covalent surface immobilization of bioactive molecules. A kinetic theory model of the biomolecule immobilization process via reactions with long-lived, mobile, surface-embedded radicals and supporting experimental data will be presented. Progress on applications of this technology to create antibody microarrays for highly multiplexed, simple analysis of cell surface markers and to engineer bioactive surfaces for implantable biomedical devices will be reviewed.


Three-dimensional (3D) biodegradable polymeric materials, such as porous scaffolds made of poly(L-lactide-co-glycolide) (PCL), have desirable bulk properties for tissue engineering, wound healing, and controlled-release drug delivery applications. However, the surface properties (e.g., chemical functionality and wettability) are often undesirable for certain biomedical applications. Therefore, the ability to fabricate 3D materials with ideal bulk properties and customizable surface properties is a critical aspect of biomaterials development. Here, we present our work on the deposition of chemically modified films throughout the 3D porous scaffold network using plasma enhanced chemical vapor deposition (PECVD). Resulting film properties can be tailored by using different precursor species. Octofluoropropane (C₃F₈) and hexafluoropropylene oxide (HFPO) precursors were chosen as model hydrophobic film PECVD systems, whereas a copolymerization system consisting of allyl alcohol (allylOH) precursor was chosen as a model hydrophilic, nitrogen containing PECVD system. To ensure the efficiency and reproducibility of the treatments, both the exterior and interior of the plasma treated scaffolds were characterized using contact angle goniometry, X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM) to assess changes in wettability, chemical functionality, and scaffold architecture in comparison to untreated scaffolds. C₃F₈ deposition on scaffolds films was found to fluorocarbon films on the exterior of the scaffold, and the extent of deposition throughout the scaffold’s 3D structure was controlled by treatment time. The nitrogen content of the allylOH/allylOH films was tailored by changing the feed gas composition of the copolymerized films. After surface modifications, modified PCL scaffold surface interactions with cells and bacteria were assessed to confirm the relevance of these coatings for the biomedical field.

We also explored the effect of different plasma treatments on cell adhesion/proliferation using both human dermal fibroblasts and endothelial cells, bacterial attachment, and biofilm formation using Escherichia coli.

5:00pm SM+AS+B+PS-ThA9 Plasma Polymerized Bandages for Wound Healing, Jason Whittle, L.E. Smith, T.L. Fernandez, University of South Australia

Wound healing is a multi-billion dollar drain on healthcare systems around the world. This is particularly true in developed countries as they deal with aging populations and conditions such as vascular disease and diabetes. More than 30% of the costs associated with treating diabetes can be attributed to management of chronic wounds. Dressings for the clinical management of wounds are constantly evolving to provide antimicrobial environments and optimal gas exchange, pH and hydration to facilitate wound healing. Ideally, the next generation of wound dressings will also provide a favourable surface for cell attachment, proliferation and migration to further promote the healing of wounds. A number of approaches have already been developed for healing chronic wounds, many of which involve culturing of explanted cells, or donor cells, and returning them to the wound site. In this paper, we have used plasma polymerisation to develop surfaces which influence the migration rate of primary cells (keratinocytes, fibroblasts and endothelial cells). A pro-migratory surface will enable cell transport into the wound bed. Earlier workers have concentrated on cell attachment as a key measurement of clinical potential, but we have observed that cell mobility exhibits a preference for different surface chemistry to attachment, and this preference depends on cell type. We show how plasma polymerization can be used to produce surfaces with controllable chemistry, and explore the effect of changing surface chemistry on the migration rate of primary fibroblasts and keratinocytes in vitro. We also investigate the effect of these surfaces on wound closure rate using an in-vitro wound healing model based on an engineered skin composite. We also explore the application of plasma polymerized pro-migratory surfaces to electrospun scaffolds for use with deeper wounds.

Scanning Probe Microscopy Focus Topic Room: 312 - Session SP+AS+BI+NS+SS-ThA

Probing Chemical Reactions at the Nanoscale
Moderator: Carl Ventrice, Jr., University at Albany-SUNY, Jun Nogami, University of Toronto, Canada

2:40pm SP+AS+B+NS+SS-ThA1 Surface Structures of Catalysts in Reactive Environments with Scanning Tunneling Microscopy, Franklin (Feng) Tao, L. T. Nguyen, University of Notre Dame

INVITED Structure and chemistry of catalysts under a reaction condition or during catalysis are the key factors for understanding heterogeneous catalysis. Advance in ambient pressure photoelectron spectroscopy has taken place over the last decades, which can track surface chemistry of catalysts in gas environments of Torr or even higher pressure. The Environmental TEM has been developed for studying structures of catalysts while they are in a gas or liquid phase. In terms of environmental TEM, images at a pressure up to bars have been obtained although 1-10 Torr to one bar is the typical pressure range of in-situ studies of catalysts by E-TEM. Compared to structural and chemical information of catalyst particles offered from environmental TEM, packing of adsorbed molecules on a catalyst surface and arrangement of catalyst atoms of catalyst surface are complementary for the structure information provided by environmental TEM. High pressure scanning tunneling microscopy (HP-STM) is the most appropriate technique to achieve these pieces of important information. With the HP-STM the structures of surfaces of model catalysts under a reaction condition or during catalysis can be tracked. Such information is significant for understanding catalysis performed at solid-gas interfaces.

In this talk, I will present the historical development of HP-STM. Then, I will review the pressure-dependent packing of chemisorbed molecules; one type of pressure dependence is the change of packing of adsorbates from site-specific binding in UHV or a gas phase with a low pressure to non-specific binding in a gas phase at a relatively high pressure; the other type is a switch binding to another specific binding site along the increase of the pressure of gas phase of the reactant. In addition, restructuring of a catalyst surface is another consequence of the increase of the gas phase pressure. The threshold pressure at which a restructuring is performed depends on the original surface structure and the intrinsic electronic state of the metal. I will review the surface restructurings of metal model catalysts including different vicinal surfaces in different reaction gases. In addition, the in-situ studies of Pt(110) and Rh(110) during CO oxidation.
oxidation will be taken as two examples to illustrate the in-situ studies of surfaces of metal model catalysts under reaction conditions (in a gas phase of one reactant) and during catalysis (in a mixture of all reactants of a catalytic reaction).

3:00pm SP+AS+BI+NS+SS-ThA3 Numerical Analysis of Amplitude Modulation Atomic Force Microscopy in Aqueous Salt Solutions, P. Karayaylal, Mehmet Z. Baykara, Bilkent University, Turkey

We present a numerical analysis of amplitude modulation atomic force microscopy in aqueous salt solutions, by considering the interaction of the microscope tip with a model sample surface consisting of a hard substrate and soft biological material through Hertz and electrostatic double layer forces (P. Karayaylal and M.Z. Baykara, *Applied Surface Science*, 2014, DOI: 10.1016/j.apsusc.2014.02.016). Despite the significant improvements reported in the literature concerning contact-mode atomic force microscopy measurements of biological material due to electrostatic interactions in aqueous solutions, the results reveal that the modest gains of imaging contrast at high amplitude set-points are expected under typical experimental conditions for amplitude modulation atomic force microscopy, together with relatively unaffected sample indentation and maximum tip-sample interaction values.

3:20pm SP+AS+BI+NS+SS-ThA4 Surface Potential Investigation of AlGAsGaAs Heterostructures by Kelvin Force Microscopy, S. Pouch, Nicolas Gervais-Walther, J. Mariolle, F. Triscone, F.M. Niquet, T. Melin, L. Borovil, CEA, LETI, MINATEC Campus, France

The Kelvin force microscopy (KFM) provides a spatially resolved measurement of the surface potential, which is related to the energetic band structure of a material. However, it depends strongly on the physical properties of the tip, e.g. width of the apex, the geometric shape and the stiffness of the cantilever as well as the surface sample state. The goal of this work is to investigate the surface potential measured by KFM on AlGAsGaAs heterostructures. For this study, we used a certified reference sample (BAM-L200), which is a cross section of GaAs and AlGaAs epitaxially grown layers with a decreasing thickness (600 nm to 2 nm) and a uniform silicon doping (5x10^14 cm^-2). The resulting stripe patterns are commonly used for length calibration and testing of spatial resolution in imaging characterization tools (ToF-SIMS, SEM, XPEEM). The surface potential measurement is performed under ultra-high vacuum with an Omicron system by using two acquisition modes: the amplitude modulation (AM-KFM), sensitive to the electrostatic force and the frequency modulation (FM-KFM), sensitive to its gradient. Three kinds of tips have been used for this study: platinum or gold nanoparticles coated silicon tips and super sharp silicon tips.

We will present the measurements obtained with these different tips for the narrowest layers (typ. < 40 nm). The surface potential mapping reveals a contrast around 300 mV between AlGaAs and GaAs layers. However, we observed that this contrast vanishes when layer thickness becomes thinner. This loss of contrast cannot be only explained by the resolution limit of the KFM technique. Indeed, we will discuss the effect of the band bending length scale at the AlGAs/GaAs interface related to the dopant concentration. The contribution of band bending between the layers is evaluated by a self-consistent simulation of the electrostatic potential, accounting for the free carriers distribution inside the sample and for the surface and interface dipoles. We will show that the electric fields of the narrowest layers recover each other, resulting in the partial or total loss of the contrast between AlGaAs/GaAs layers. The simulation results will be compared to the experimental results in order to emphasize that the surface potential contrast is not only influenced by the resolution limit.

4:00pm SP+AS+BI+NS+SS-ThA6 Probing the Quantum Nature of Hydrogen Bonds at Single Bond Limit in Interfacial Water, Ying Jiang, Peking University, China

INVITED

Quantum behaviors of protons in terms of tunneling and zero-point motion have significant effects on water properties, structure, and dynamics even at room and at higher temperature. In spite of tremendous theoretical and experimental efforts, accurate and quantitative description of the quantum nuclear effects (QNEs) in water is still challenging, due to the difficulty of accessing the internal degrees of freedom of water molecules. Using a low-temperature scanning tunneling microscopy (STM), we are able to resolve in real space the internal structure, that is, the O-H directionality, of individual water molecules adsorbed on a solid surface [1,2]. The key steps are decoupling electronically the water from the metal substrate by inserting an insulating NaCl layer and enhancing the molecular density of states of water around the Fermi level via tip-water coupling. These techniques allow us not only to visualize the concerted quantum tunneling of protons within the H-bonded network, but also to determine the impact of proton delocalization on the strength of hydrogen bonds by resonantly enhanced inelastic electron tunneling spectroscopy (IETS).

Key words: STM, IETS, water, QNEs, proton transfer, H-bonding strength


4:40pm SP+AS+BI+NS+SS-ThA8 Resonant Enhanced Spectroscopy of Molecular Rotations with the STM and Field Effect Control of Molecular Dynamics, Fabian Natterer, F. Patthey, Fabian Natterer, E. G. Wang, Nature Communications 5, 4056 (2014).


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**Surface Science**

**Room:** 309 - Session SS+AS+NS-Th-A

**Semiconductor Surfaces and Interfaces 1**

**Moderator:** Ludwig Bartels, University of California - Riverside, Kurt Kolasinski, West Chester University

2:20pm SS+AS+NS-ThA1 A Study of the InAs(001) Surface Electronic Structure, Jacek Kolodziej, N. Tomaszewska, P. Ciochon, Jagiellonian University, Poland

Angle-resolved photoelectron spectroscopy (ARPES) is used to study electronic bands at the n-type InAs(001) surfaces, having several different reconstructions. Indium-rich-rich (8x2)/(4x2) and antimony-rich (2x2)/(2x4) surfaces as well as sulphur passivated (2x1) surface are prepared and investigated. Measured electronic bands are identified by analysis of their symmetries in the k-space.

In InAs crystal bulk the conduction band minimum (CBM) is located very close to the Fermi level (FL). Downward band bending, typical for the studied surfaces, causes formation of two dimensional electron gas, confined in a subsurface well, also known as the electron accumulation layer. This is indicated by characteristic quantized subband states visible in the ARPES spectra.

It is shown that the band bending magnitude and the quantization (of the accumulated electron energies associated with the coordinate normal to the surface) depend on the surface reconstruction as well as on the crystal doping. In most cases the electron accumulation bands are found at the Fermi level and low the Γ_{15} symmetry point in the center of the surface Brillouin zone. The most clear picture is observed for sulphur passivated (2x1) surface, where three distinct subbands with minima at E_F=-0.276eV, E_F=-0.096eV and E_F=-0.039eV with reference to Fermi level are found.

**Surface Science**

**Room:** 309 - Session SS+AS+NS-Th-A
and semiconductor. However, there has been a debate on possible GaAs that could produce device-quality electrical interfaces between the oxide insulator/III-V semiconductor interface. Gallium oxides on GaAs represent one of contenders for suitable surface passivated oxide-based dielectrics suitable surface passivation technology for fabrication of high quality (MISFETs) have been re-ignited recently due to the approaching of the Interests in metal-insulator-semiconductor field effect transistors scaling limit of Si complementary metal-oxide-semiconductors (CMOS).

formation of both Ga2O and Ga2O3 is observed with the extent of oxidation in the order of NO>O2>N2O at elevated pressures. At elevated temperatures, charged oxygen interstitial motion within the ZnO indicates that the near-surface concentration of these defects scales quadratically with VS, thereby pointing to a novel general approach by which bulk point defect concentrations can be controlled.

3:00pm SS+AS+NS-ThA3 Evolution of Surface-Assisted Oxidation of GaAs by Gas-Phase N2O, NO and O2 Xueqiang Zhang, S. Ptaslinska, University of Notre Dame

Interests in metal-insulator-semiconductor field effect transistors (MISFETs) have been re-ignited recently due to the approaching of the scaling limit of Si complementary metal-oxide-semiconductors (CMOS). The understanding of the III-V semiconductor oxides is important for the availability of suitable surface passivation technology for fabrication of high quality insulator/III-V semiconductor interface. Gallium oxides on GaAs represent one of contenders for suitable surface passivated oxide-based dielectrics that could produce device-quality electrical interfaces between the oxide and semiconductor. However, there has been a debate on possible GaAs oxides and their mechanisms over years. A comparative study between O2 and other reactive but heteronuclear molecules (such as NO and N2O) near realistic conditions would provide new insights for a better understanding of the GaAs oxidation process.

A near-ambient pressure X-ray photoelectron spectroscopy (NAP XPS) study of interfacial chemistry between GaAs (100) and three oxidizing gases, N2O, NO and O2, are carried out in a wide range of pressures and temperatures. At room temperature, surface oxidation, involving the formation of both GaO and Ga2O3, is observed with the extent of oxidation in the order of NO>O2>N2O at elevated pressures. At elevated temperatures, the extent of oxidation is in the order of O2>NO>N2O. Our experimental results show that the oxidation of GaAs (100) by N2O and NO is primarily determined by the probability and nature of interactions at the gas/surface interface, whereas the limiting factor in the case of O2 is the energy requirement for O=O bond dissociation.

3:20pm SS+AS+NS-ThA4 Morphology Dependence of Gas-Phase Molecule Interactions with GaAs Surfaces, Sylvia Ptaslinska, X.Q. Zhang, University of Notre Dame

A great deal of progress has been made in understanding molecular interactions at the interface of two-dimensional GaAs systems under ultrahigh vacuum (UHV) conditions. While research on understanding of such interactions with lower-dimensional GaAs-based structures, such as one-dimensional nanowires (NWs), has not been performed despite the potential importance of these structures for developing nano-electronic circuits. Moreover, surface characterization of GaAs under more realistic than the UHV studies, are critical in any attempt to correlate surface chemistry with device properties.

Nowadays, due to recent developments in the surface characterization techniques, and especially the development of Near Ambient Pressure X-ray Photoelectron Spectroscopy (NAP XPS) [1], we are able to track surface chemistry in-situ under elevated pressures and temperatures for different morphologies.

In our present study we used NAP XPS to investigate the interaction of a radially non-planar GaAs surface comprised of an ensemble of GaAs NWs with O2 and H2O molecules. In this study the evolution of O2 and H2O molecule dissociation on GaAs NWs is tracked under in-situ conditions as a function of temperature and gas pressure to establish whether these processes depend on surface morphology. In contrast to ideally flat GaAs single crystal surfaces that are previously studied [2], gas molecules experienced the enhanced dissociation on GaAs NW ensembles due to an increase in the surface area ratio and the presence of stepped edges, atom vacancies, and other defects on non-flat semiconductor surfaces [3].


4:00pm SS+AS+NS-ThA6 STM Imaging of the Buried Interface Structures at Ultra-thin Ag Films/Si(111) Substrates, Y. Yoshikti, I. Kokubo, Y. Aoki, K. Nakatsuji, Hiroyuki Hiyarama, Tokyo Institute of Technology, Japan

The Schottky barrier height (SBH) has been reported to change sensitively to the variety of reconstructions at the Si substrates before depositing metal films in such systems as Pb/Si(111) and Ag/Si(111). Meanwhile, metal and Si do not mix, and the interfaces between the metals films and Si substrates are abrupt in these systems. Thus, reconstructions on (111) substrate are regarded to be preserved at buried interfaces under metal films, and have an influence on the SBH. In this respect, direct characterization of the buried interface structures in real space is required.

Scanning tunneling microscopy (STM) is a potentially promising method to achieve this, although it is conventionally considered to be useful only for exposed surfaces. Substantially, two different patterns, which were regarded to reflect the periodicity of the lattice at the buried interfaces, were observed on Si(111)7x7 films on the (111) substrate. However, the relation to the buried interface structures and the reason for the visualization were still not elucidated. With regard to these points, it is of significant interest to examine whether a different reconstruction on the Si(111) substrate could cause various periodic patterns in abrupt interface systems other than the Pb/Si(111). It is also of interest to investigate the origin of the new periodic pattern. From this perspective, we investigated the STM images of ultra-thin Ag films on Si(111)3x3-v3-B and Si(111)7x7 substrates in this study.

As results, ripples were observed at the surface of ultra-thin Ag films on a Si(111)3x3-v3-B substrate in STM and dI/dV images. The ripples were faint, independent of the bias voltage, and had the 3x3 periodicity. These indicate that the ripples were geometric corrugations formed at the Ag film surface, which were induced by the commensuration of the Ag(111)1x1 and Si(111)3x3-v3-B lattices at the buried interface. In the mean time, different ripples were observed on Ag films on a Si(111)7x7 substrate. The ripples were less periodic, but the Fast Fourier Transform of the images revealed that they had the 7x7 periodicity. In contrast to the Pb/Si(111)7x7 system, the ripples were independent of the bias voltage. Thus, the 7x7 ripple was also regarded to reflect the interface commensuration-induced geometric corrugations at the Ag film surfaces.

More detailed results and Synchrotron radiation X-ray diffraction data of these buried interfaces will be shown and discussed in the presentation.

4:20pm SS+AS+NS-ThA7 Ge on Si Epitaxy: Formation of 3D Ge Islands on Si(100)-2x1 by Annealing of Ge Wetting Layers, Gopalakrishnan Ramalingam, P. Reinke, University of Virginia

The epitaxial growth of Ge on Si(100)-(2x1) proceeds by Stranski-Kratanow (SK) mode where the formation of a wetting layer (WL) is followed by the emergence of quantum dots (QD). New growth modes have been recently reported to lead to highly anisotropic Ge NWs and are achieved by annealing of the WL prior to the onset of QDs. The goal of the current work is to understand the atomistic processes involved in the transformation of the WL during annealing. We have investigated the WL structure during post-growth annealing at 400 to 600 °C and the transformation of epitaxial two dimensional Ge wetting layers into three dimensional Ge islands, referred to here as pre-quantum dots (p-QDs). The p-QDs include hillocks with a stacked, wedding-cake type structure which show a progression to partial [105] faceting in case of thicker Ge WLs and longer anneal times. At low WL thickness (1-1.5 ML), the p-QDs have a stacked structure while thicker WLs (2-3.5 ML) lead to partial [105] faceting.
faceted structures. All p-QDs, irrespective of the faceting or size, are characterized by an amorphous mound at the apex; this is strictly limited to p-QDs not observed for regular QDs. The transition from the WL to p-QDs depends sensitively on the WL thickness (for a given annealing temperature): a six-fold increase in the island number density and a similar decrease in average island volume are observed when the initial WL thickness was increased from 1.2 to 3.5 ML. A small but notable increase in the island number density is observed when samples are annealed for longer durations (after the initial anneal to form the p-QDs) confirming that Ostwald ripening is not a dominant process in this system. Our observations will be integrated with a simulation of the growth process which will inform on the relevant mass transport and the role of strain on the WL transformation to p-QDs.

4:40pm SS+AS+NS-ThA8 In Search of Nanopatterns: STM Provides Mechanistic Insights into Silicon Functionalization. Erik Skibinski, Cornell University. DeBenedetti, Y.J. Chabal, University of Texas at Dallas, M.A. Hines, Cornell University

Functionalization reactions leave characteristic patterns on surfaces that can be read by STM, providing insight into reaction mechanisms. The functionalization of silicon surfaces with organic monolayers has attracted interest for applications ranging from chemical and biological sensing to renewable energy. A wide variety of surface functionalization reactions have been developed based on dehydration reactions that target surface -OH groups on oxidized silicon. Uniform functionalization therefore requires a uniform, high density of surface –OH groups. Hydroxylation silicon surfaces without concomitant oxidation of the substrate was long thought impossible; however, a novel three-step strategy was recently reported.1 A hydrogen-terminated silicon surface is first methoxylated in methanol, and then the Si–OCH3 sites are converted first to Si–F then to Si-OH by successive immersion in hydrofluoric acid and water. Original spectroscopic evidence suggested the creation of nanopatterned surface, in which every other site on the surface is functionalized. New STM and spectroscopic data show selective reaction at step edges and an unexpected functionalization pattern. The mechanistic implications of this pattern will be discussed.


5:00pm SS+AS+NS-ThA9 Benzene and Chlorobenzene Dissociation Pathways Involving Singlet-Triplet Crossing on the Si(100) Surface Modeled Using Small Clusters. Nicholas Materer, E. Butson, Oklahoma State University. Q. Zhu, University of Pittsburgh

The dimer rows in the Si(100) surface have di-radical character, which can be configured as a singlet or triplet. At the minimum energy crossing point of the singlet to triplet crossing for a single Si-dimer cluster, the spin-orbit coupling (SOC) coefficient was determined to be approximately 25 cm⁻¹. Using this SOC, the Landau-Zener spin-crossing probability at room temperature was computed to be approximately 0.5%. Similar computational methods were used to investigate possible adsorption and dissociation processes for benzene and chlorobenzene. The 1,2 product (a tilted configuration) for benzene adsorption was proposed to undergo C-H bond cleavage to form lower-energy products. However, this process requires a spin-crossing of the initial 1,2 bond product, followed by a transition state with large activation barriers. Chlorobenzene can absorb on the Si(100) by breaking one double bond on the phenyl ring and forming two new carbon-silicon bonds with the dimer cluster. Again, for dissociation to occur, the system must undergo a spin crossing process from the singlet to the triplet state. After this spin crossing event, the carbon-chlorine bond is cleaved and a new silicon-chloride bond is formed. The final product is a dissociation product with chlorine and a phenyl ring attached directly to the (100) surface of silicon. Both cases illustrate that spin crossing could be more common than realized in the adsorption and dissociation of organic molecules on Si(100).

5:20pm SS+AS+NS-ThA10 Adsorption of Organic Triols on Ge(100)-2x1 Surface. Tania Sandoval, S.F. Bent, Stanford University

Organic functionalization of semiconductor surfaces can provide tunable control of interfacial properties in organic-inorganic hybrid devices. The key step toward applications in this area is to understand the selectivity in the reactions of organic molecules on these surfaces. In this work, adsorption of 1,3,5-benzenetriol and 2-hydroxymethyl-1,3-propanediol on Ge(100)-2x1 surface was studied. Both molecules have three hydroxyl groups available for reaction with the Ge surface. While the reactions of these molecules with the surface may be similar, differences in reactivity can be expected due to their different backbone structures. The aim of this study is to investigate whether a difference in reactivity exists and how the reaction with the surface is affected by the structure of the molecules.

Energy diagrams for both molecules were calculated by density functional theory. In both cases, proton transfer reactions from two or three hydroxyl groups to the Ge dimer atoms are suggested as thermodynamically favored pathways. However, the reaction through 3 OH groups in 2-hydroxymethyl-1,3-propanediol is more than 15 kcal/mol more stable than the same reaction in 1,3,5-benzenetriol. This difference can be associated with strain of the aromatic ring.

Infrared spectroscopy (IR) and X-ray photoelectron spectroscopy (XPS) were performed to investigate the adsorption products. IR results show the presence of a ν(Ge-H) mode for both molecules, suggesting the proton transfer reaction as the main pathway. XPS spectra of each molecule both chemisorbed and physisorbed on the surface were obtained. The differences between these two spectra can be used to indicate the reaction products. For both molecules, no change in the C(1s) spectra is observed, suggesting that carbon does not form a bond directly with Ge. On the other hand, clear differences between the chemisorbed and physisorbed O(1s) spectra are observed for both molecules. A second peak with a lower binding energy only in the chemisorbed spectra, assigned to a Ge-O bond confirms that both molecules react with the Ge surface through O-H dissociation. The ratio between O(1s) peaks indicates that about 80% of the total hydroxyl groups are involved in reaction with Ge, suggesting that a significant fraction of the adsorbates react with the surface through all 3 of their hydroxyl groups.

In conclusion, both 1,3,5-benzenetriol and 2-hydroxymethyl-1,3-propanediol react with the Ge(100)-2x1 surface through O-H dissociative adsorption. Little difference in reactivity was observed between these triols, suggesting that other factors besides backbone structure are governing the reactivity in these systems.

77 Thursday Afternoon, November 13, 2014

Formation and growth of Pt, Rh, and Pd nanoclusters on a graphene covered metal substrate has been investigated by ultrahigh vacuum scanning tunneling microscopy (UHV-STM). For this purpose a graphene film was formed on the Cu (111) surface by the decomposition of ethylene at high temperatures. According to our results, isolated graphene islands were successfully grown on the Cu surface with different periodicities. Different rotational domains were observed as a result of weakly coupled Cu and graphene caused by the low C solubility in Cu. The most prevalent moire patterns have periodicity of 2.2, 4 and 6.6 nm with rotational angles of 0° and 1.4°, and 37°. Subsequently, nanoclusters were formed at room temperature on the template of a graphene moire pattern formed on Cu (111) surface. As confirmed by the height and size profiles, Rh and Pt clusters display similar planar structures with an average height of about 0.4 nm and average diameter of about 10 nm. The size and distribution of the metal clusters on the two types of Moiré seem to be different. The clusters on the smaller Moiré pattern show a narrow size distribution in both diameter and height. Additionally, these nanoclusters are found to be relatively stable and only undergo agglomeration at relatively high temperatures. These results demonstrate that the metal-C and metal-metal interactions may play a significant role in the cluster formation and it is possible to fabricate finely dispersed metal nanoclusters on the moire structure of graphene covered Cu (111).

AS-ThP2 Valence Band Offsets of Two Rare Earth Oxides on AlGaN, n(N (025)<0.67) as Measured by Photoelectron Spectroscopy. Michael Brunbach, A. Alleran, D. Wheeler, S. Alcicyt, J. Bielefeld, Sandia National Laboratories

Preparation of high quality gate oxides on wide bandgap semiconductors is a challenge for realizing efficient high performance devices. For GaN electronics there are a limited number of compatible oxides that have a sufficiently large bandgap to minimize electrical leakage. In this work, reactive molecular beam epitaxy was used to deposit rare earth oxides, Gd2O3 and La2O3, on GaN substrates. For Gd2O3, the valence band offset was tuned by altering the composition of the AlGaN substrate. Thin films were characterized using reflection high-energy electron and X-ray diffraction and valence band offsets were determined via X-ray photoelectron spectroscopy.

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-ThP3 Surface Electronics of Individual Si-doped GaN Wires Studied by Synchrotron-Radiation XPEEM Spectromicroscopy. Olivier Renault, N. Chevalier, J.W. Morin, CEA-LETI, France

Heavily Si-doped GaN wires are at the basis of innovative LEDs used in advanced solid-state lightning. Understanding how silicon incorporation influences the electronic properties and the measured electrical characteristics of recently emerged very high-conductivity GaN wires [1] is of prime importance for future device optimization.

Here, we have implemented photoemission microscopy with synchrotron radiation (XPEEM) [2] and scanning Auger nanoprobe microscopy (SAM) [3] to investigate the incorporation of Si at the surface of individual GaN wires of 2 µm diameter and the local work function. The high-resolution Si2p micro-spectra evidence complex incorporation of Si pointing on intentional (Si substitution in Ga sites) and un-intentional doping (Si substitution in N-vacancies). By combining elemental analysis from SAM and XPEEM core-level results, we can quantitatively discriminate these two contributions to the doping. Next, we have studied the influence of illumination flux on both the work function and Ga3d binding energies, the strong variations of which evidence surface band bending through the surface photovoltaic effect.

This work was carried out at the NanoCharacterization Platform (PFNC) of MINATEC.

AS-ThP6 Characterization of Nanostructured Cu-Zn Oxides Used for Photocathodic Water Splitting. Sankar Raman, J.F. Moulder, Physical Electronics Inc., S. Banarjee, Washington University, St. Louis, Y. Myung, H. Park, P. Banarjee, Washington University, St. Louis

Metal alloys can be efficiently exploited, via controlled fabrication steps, to create mechanically robust and adherent, mixed metal oxide films with tunable photoelectrochemical (PEC) properties. Brass, an alloy of Cu and Zn is an inexpensive source of semiconducting Cu2O, CuO and ZnO, which have all been used separately as photo-cathodes or photo-anodes respectively for solar water splitting. However, thermodynamics and free energy change predicts a prevalence of ZnO formation when brass is oxidized. We have co-fabricated Cu and Zn oxides to form a highly adherent, mixed metal oxide surface and investigated the relationship between structure property and performance in a PEC cell.

Structural and chemical characterization of the oxide layer was accomplished using an SEM and the PHI X-Tool Scanning XPS microprobe. SEM results show the presence of CuO nanowires interspersed with ZnO fibers and high energy resolution XPS provides detailed chemical state information for Cu and Zn on the surface as a function of sample treatment.

This study indicates that the thermal oxidation of metal alloys can lead to formation of highly interspersed, mixed oxide phases forming novel heterojunctions for use as economical and manufacturing-scalable energy harvesting devices.

AS-ThP8 Impact of a Mixed Oxide’s Surface Composition and Structure on Its Adsorptive Properties: The Case of the α-(Fe,Cr)2O3(0001) Surface. M.A. Henderson, Mark Engelhard, Pacific Northwest National Laboratory

Characterization of an α-(Fe0.75,Cr0.25)2O3(0001) mixed oxide single crystal surface was conducted using x-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), low energy electron diffraction (LEED) and temperature programmed desorption (TPD). After sputter/anneal cleaning in ultra-high vacuum (UHV), the mixed oxide surface became terminated with a magnetic-(111) structure based on the presence of (2x2) spots in LEED and Fe2+ in XPS. The composition of the surface was close to that of α-Mo2O3 based on XPS, with the metal (M) content of Fe2+ and Cr3+ being close to 1:4:1, despite the fact that the film’s bulk was 3:1 with respect to the metal cations. The enrichment of the surface with Cr was not altered by high temperature oxidation in UHV, but could be returned to that of the bulk film composition by exposure to the ambient. Adsorption of various probe molecules (NO, O2, CO2 and H2O) was used to identify the active cation sites present in the (Fe,Cr)2O3(111) terminated surface. Although XPS and SIMS both indicated that the near-surface region was enriched in Cr3+, no adsorption states typically associated with Cr3+ sites on a Cr2O3 single crystal surfaces were detected. Instead, the TPD behaviors of O2 and CO2 pointed toward the main active sites being Fe2+ and Fe3+, with O2 preferentially adsorbing at the former and CO2 at the latter. NO was observed to bind at both Fe2+ and Fe3+ sites, and H2O TPD looked nearly identical to that for H2O on the Fe3O4(111) surface. Competition for adsorption sites between coadsorbed combinations of CO2, O2, H2O and NO corroborated these assignments. These results indicate that the surface composition of a mixed oxide can vary significantly from its bulk composition depending on the treatment conditions. Even then, the surface composition does not necessarily provide direct insight into the active adsorption sites. In the case of the (Fe,Cr)O2(111) termination of the α-(Fe0.75,Cr0.25)2O3(0001) surface, Cr3+ cations in the near-surface region appear to be fully coordinated and unavailable for adsorbing molecules.

AS-ThP9 Analysis of Metal Particles by Proximal Excitation of Al and Mgk X-rays. C.F. Mallinson, James Castle, University of Surrey, UK

In preliminary work [1] we have shown that use of an aluminum substrate to support a distribution of copper particles enables their characteristic photoelectrons to be observed within the Auger electron spectrum generated by an incident electron beam. This observation raises the possibility of the use of chemical shifts and the corresponding Auger parameter to identify the chemical states present on the surface of individual sub-micrometer particles within a mixture. In this context, the technique has an advantage in that the Auger electron spectroscopy, the electron Auger electron spectroscopy, the electron beam does not dwell on the particle but on the substrate adjacent to it. Given the importance, for both medical and toxicological reasons, of the surface composition of such particles we have continued to explore the potential of this development.
In this contribution, we show that proximal excitation of x-rays is equally successful with magnesium substrates: In some regions of the XP spectrum the nearly larger Auger peaks generated by the electron beam can cause inconvenient clustering of Auger and photoelectron peaks. As in conventional XPS, the ability to switch between Al and Mg sources is useful in such situations. In this context, we have extended the studies to iron and nickel particles where we show that use of Al or Mg substrates, as necessary, can make a contribution to clear identification of individual components in the Ni 2p peaks.

For this development in electron spectroscopy to achieve its full potential it is necessary to optimise the beam conditions used to generate the local x-ray to give good selectivity of a given particle. Measurements made in support of this will be given. Of greater concern is a possible problem of local heating associated with x-ray generation. We continue to explore this problem and report some progress in minimising heating of the particle whilst maintaining the particle selectivity that is central to this exciting development.

References

Thin polymer films are found in an enormous range of devices and have many applications from use in semi-conductors, displays and solar cells to corrosion protection and packaging. New ion sources such as the multi-mode Ar gas cluster ion source (GCIS) have revolutionised the study of such organic thin films by depth profiling with techniques such as X-ray photoelectron spectroscopy (XPS). As reported elsewhere the chemical composition of organic thin films may now be determined as a function of depth by a combination of XPS analysis and etching using massive Ar ions.
In this study we present results from XPS gas cluster depth profiling of multi-layer organometallic thin films. The multi-layer structures are formed by sequential immersion of a pyridine-terminated template layer on silicon or ITO-coated glass substrates.

Parasitic friction in internal combustion engines accounts for 10-15% of the nearly 7 billion barrels of oil consumed by cars and trucks in the United States. Recently a new group of oil-miscible ionic liquids has been developed as next-generation lubricant additives. Among the many positive attributes of these IL-additives are thermal stability, excellent wettability, non-corrosive, and most importantly, they possess effective anti-scuffing/anti-wear and friction reduction characteristics. Since the idea of using ionic liquids (ILs) as lubricants was raised in 2001, many studies have been conducted in this area and results have demonstrated superior lubrication performance for a variety of ILs. It is widely believed that a protective tribo-boundary film is formed on the contact area by tribochemical reactions between the metal surface and the IL during the wear process and, as a result, reduces friction and wear. However, the study of this critical boundary film in the literature has been limited to two-dimensional topography examination and chemical analysis from the top surface. Several ionic liquids have been evaluated in both bench and engine tests at ORNL and have shown superior wear protection compared to conventional anti-wear additives. In this poster, two IL (N888H][DEHP] and [P888][DEHP]) have been used in scuff tests of cast iron samples (pin-on-disk arrangement) and are compared with zinc dialkyldithiophosphate (ZDDP). The most common anti-wear additive. X-ray photoelectron spectroscopy (XPS) was first used to examine chemical bonding in the ionic liquids and the ZDDP in their liquid state. This is possible due to the extremely low vapor pressure exhibited by these materials (including ZDDP). The scuff tests produce tribo-films on the cast iron samples. XPS depth profiling is used to determine the composition as a function of depth for these tribo-films. Chemical bonding within the tribofilm is compared and contrasted to the photoemission results obtained on the liquid forms of the IL’s and ZDDP.


X-ray Photoelectron Spectroscopy (XPS) is well known for its surface specificity and chemical selectivity. By studying the small binding energy shifts of core level spectra, the analyst may identify the chemical bonding environments of elements present in the surface. When electronic structure or valence information is required, however, many analysts will turn to Ultraviolet Photoelectron Spectroscopy (UPS). There have been many publications in the literature which demonstrate that XPS can also provide electronic and valence information, ranging from work function measurements to valence bonding information.
This work demonstrates the utility of XPS for such measurements and compares results from the same sample set using the complementary techniques of XPS and UPS.

An understanding of material interactions and degradation pathways in both fielded modules and modules used for accelerated testing is important for photovoltaic (PV) materials specification. As part of the effort to build this understanding, a suite of destructive and non-destructive testing protocols has been developed to compare material performance and reliability under the stresses of different service environments.
This presentation will describe our recent experience mapping the physical and chemical changes observed in degraded PV modules. Examples will include: a) the application of Laser Ablation–Inductively Coupled Plasma–Mass Spec (LA-ICP-MS) for the study of ion migration pathways in encapsulants after PID (Potential Induced Degradation); b) Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) to follow chemical changes in cells extracted from modules following PID and Damp Heat exposure; and c) NanoHardness testing (NHT) to map mechanical property differences in backsheet structures removed from PV modules after field exposure.

AS-ThpP14 Surface and Interface Studies of Flexible Front Sheets for PV Modules, Lei Zhang, N.J. Glassmaker, B.B. Sauer, DuPont Central Research and Development
To develop the next generation flexible front sheets for photovoltaic (PV) modules, FEP, a tetrafluoroethylene/TFE copolymer with ~10wt% hexafluoro propylene, has shown great promise due to its low refractive index and superior properties in light transmission. The chemical and photochemical inertness of FEP make it an ideal candidate for PV front sheets; FEP is expected to produce approximately ~1.5% to ~5% improvement in module power output over incumbent glass or poly(co-ethylene-tfe) (ETFE) front sheets.
Because FEP is a per-fluorinated polymer, the grand challenge in the development process is to achieve good adhesion between the FEP film and the underlying poly(co-ethylene-vinyl acetate) (EVA) encapsulant layer. The adhesion of glass and ETFE to EVA has been demonstrated to be durable to environmental effects. However, untreated FEP film has poor adhesion to EVA, especially after accelerated weathering test conditions at elevated temperature and humidity. In order to exploit the advantages that FEP can offer for improved module efficiency, we have developed a multi-step treatment process to modify FEP surfaces for enhanced adhesion of FEP to EVA. Integrated analytical techniques including XPS, contact angle, SEM, and others were applied to characterize the complex surfaces and interfaces of the modified fluoropolymer surfaces. These analytical results have helped us to better understand the treatment induced functionality on the FEP surfaces, especially the possible mechanism and the locus of failure at the FEP-EVA interface. This presentation will focus on the studies of the modified FEP-EVA surfaces/interfaces and their correlation with adhesion performance.

AS-ThpP15 Multi-technique Surface Analysis of Catalytic Systems with UPS, ISS and UPS, Bill Sgammato, Thermo Fisher Scientific, UK
Characterization of catalytic systems benefits from analysis with multiple surface analysis techniques. X-ray Photoelectron Spectroscopy (XPS), for example, is the ideal technique for identifying different chemical species present within the top 10nm of a catalyst surface, but if the elemental composition of the top monolayer is to be investigated then Ion Scattering Spectroscopy (ISS) is the preferred analytical technique. Additionally, if the surface electronic structure can be analyzed, using Ultraviolet Photoelectron Spectroscopy (UPS), then it may be possible to correlate catalytic activity
with electronic structure enabling the analyst to identify the chemical species and active sites responsible for catalytic reactions. This work demonstrates how a single, multi-technique surface analysis system can be used to comprehensively characterize a catalytic system. XPS, ISS and UPS data is presented.


A fundamental understanding of the surface chemistry of chemical warfare agents is needed to fully understand the interaction of these toxic molecules with militarily relevant materials. Knowledge of the surface chemistry of agents can be applied to the creation of next generation decontaminants, reactive coatings, and protective materials for the warfighter. Here, we describe a multi-functional ultra-high vacuum instrument for conducting comprehensive studies of the adsorption, desorption, and surface chemistry of chemical warfare agents on model and militarily relevant surfaces. The system applies reflection-absorption infrared spectroscopy, x-ray photoelectron spectroscopy, and mass spectrometry to study adsorption and surface reactions of chemical warfare agents. Several novel components have been developed to address the unique safety and dosing issues that accompany the research of these toxic, often very low vapor pressure, compounds. Equipment and methods applied in order to safely work with chemical warfare agents will be detailed.


Analysing key components of technologically significant devices such as OLED displays, Li-ion batteries and catalyst materials can present challenges to the surface analysts. Amongst the most critical issue is the air sensitivity of these materials. Small amounts of oxygen or water vapour can cause radical changes in the material, ultimately affecting the analysis results and leading to uncertainty in the validity of any conclusions drawn. Transfer from the preparation environment to the instrument requires the samples to be loaded into a container that can be unloaded into vacuum in the analysis instrument without exposure to the ambient atmosphere. In this presentation we will show results obtained using a new transfer vessel, designed to make the introduction of samples into the vacuum system more automated. Data has been collected from samples covering a range of application areas in order to validate the system, and this will be used to illustrate the benefits of the design.

AS-ThP18 Large-Area Secondary Ion Mapping: An Essential Component of Industrial Problem-Solving. Kathryn Lloyd, J.R. Marsh, DuPont Corporate Center for Analytical Sciences

Secondary Ion Mass Spectrometry (SIMS), carried out with liquid metal primary ion sources and time-of-flight mass analyzers, has long been recognized as a means of obtaining lateral distributions of species at the surface via detection of chemically-specific molecular ions. As efforts continue to routinely achieve sub-micron lateral resolution from organic and electrically-insulating samples, it is worth noting that the technique easily lends itself to large-area (millimeters to centimeters) chemical mapping. This capability fills an important niche in the chemical mapping “toolbox” and is relevant to many industrial surface-related problems.

For small-area (less than 500x500 µm²) mapping, the primary ion beam optics are (usually randomly) rastered across a pixel array spanning the area of interest, and secondary ion spectral data is collected at each pixel. In the simplest implementation of large-area mapping, the sample stage is moved in regular (essentially large pixel) intervals under an optically-stationary primary ion beam. A more optimal approach is to combine both small-area ion beam rastering with stage rastering in a so-called “patch” configuration. These large-area mapping acquisitions typically take 30 minutes. Coupled with multivariate analysis, they provide a chemical view of the surface not easily obtainable from other techniques. Examples shown will include optimization of anti-stick coating, understanding fabric color streaking, and assessment of printing uniformity.

AS-ThP19 In Situ Ar Plasma Cleaning of Samples Prior to Surface Analysis. Vincent Smentkowski, H. Piao, General Electric Global Research Center, C.A. Moore, KEI Scientific

The surface of as received samples is often contaminated with adsorbed layers of hydrocarbons. These surface contaminants can attenuate or mask underlying species of interest, inhibiting or compromising accurate analysis. In-situ ion beam sputtering is often used to remove the outer layer of a sample surface and thus remove contaminants, however this erosion process is inherently destructive and can alter the surface of interest. Moreover there are also many materials that can not be cleaned using monoatomic ion beam sputtering as the material(s) may decompose and deposit a layer of fragments onto the outer surface of the material to be analyzed. Recently gas cluster ion beams (GCIB) have been developed, which allows for depth profile analysis of organic layers with minimal degradation (and references therein). GCIBs have also been used for low damage surface cleaning6,7. A non-line-of-sight protocol which is able to clean large (mm or greater) areas is desired. We recently demonstrated that ambient air plasma processing can be used to clean the outer surface of samples8, however ambient air plasma treatment can result in oxidation of the material. In this presentation we report our first attempts at in-situ plasma cleaning of samples using Ar prior to XPS and ToF-SIMS analysis. We compare Ar plasma cleaning with air plasma cleaning, and report key findings.


Accurate characterization of ultra-thin surface films is a basic requirement for the successful development of the electronic devices. For example, electrical transport measurements in molecular electronics, often consisting of ultra-thin films, are extremely sensitive to the quality of the films and their associated interfaces. As an experimental technique, X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. However, interpretation of the raw experimental data requires a reliable theoretical modeling of the photoelectron attenuation; a mechanism that is usually addressed by considering a continuum medium with a phenomenological attenuation parameter. Such models impose severe limitations when self-assembled molecular layers (SAMs) are to be analyzed. In SAMs studies, calculations based on a Discrete Distribution Profile (DDP) are necessary for a proper accounting of atoms situated at the specific locations along the molecular backbone.

In this work, 1-undecane, 11-chloro monolayer deposited on Si substrate was used as a model system. XPS intensities of carbon, chlorine, oxygen and silicon were measured and their components (C₆H₁₃, Cl, O, Si) were quantified using curve fitting analysis. The intensity ratios (C₆H₁₃/Cl, C₆H₁₃/O, C₆H₁₃/Si) were then compared to DDP calculated ratios, yielding excellent agreement between experimental and calculated values. The detailed agreement points to the high quality of the studied layers and, more generally, supports the validity of the DDP model as a tool for thin films characterization.


Thin film solar cells rely upon the efficient transfer of photocharge from the absorbing photovoltaic material to an external circuit via thin buffer junction layers. Problems such as low fill factor and current loss arise when the electron collecting contact (emitter) exhibits a large positive conduction band discontinuity with the absorber. This study shows evidence for one approach to circumvent this problem by taking advantage of electronic defects present in chemical bath deposition (CBD) of buffer layers. X-ray and ultraviolet photoelectron spectroscopy (XPS/UPS) of heterojunctions formed between CZTSe and CBD-ZnOS with two different buffer preparations exhibit clear differences in electronic properties yet we observe no discernable differences in composition. Structure of CBD-ZnOS made using the different preparation methods is measured with grazing incidence X-ray diffraction (GIXRD) and also exhibits no discernable
differences in the peak positions or full widths. XPS/UPS derived band energy diagrams are presented for quasi-in-situ prepared CZTSe/CBD-ZnO interfaces with both preparation methods yielding valence band offsets equal to -1.0 eV and conduction band offsets equal to 1.1 eV. However, comparison between water only and a water/dimethyl sulfoxide solvent mixture in device characterization and band offset measurements show increased band bending in accordance with higher n-type carrier density with water as the only solvent. Seemingly incongruous, the more strongly n-type buffer layer performs worse in solar cells and exhibits inflected current-voltage response under one-sun illumination. A proposed electron transport band for these buffer layers that seems to circumvent the large conduction band spike is estimated to have energies about 0.6 eV below the conduction band of the CBD-ZnO. Hence, these defects appear to enable adequate band-lineup with the low-band gap absorber, CZTSe ($E_G = 0.96$ eV). These findings suggest that cosolvent approaches may allow for the manipulation of the electronic structure of ZnO and enable a wider range of electronic applications where larger electron affinities are required.

**AS-ThP25 Analysis of Metal Nanoparticles by Auger, XPS and TEM. Wayne Jennings, Case Western Reserve University, C.V. Bishop, The Best Mode Company, J. Cowen, Case Western Reserve University, J.S. Hammond, D.F. Paul, Physical Electronics USA**

Nanoparticles of Pd and PdSn are important as catalysts for chemical reactions and metallization of polymeric materials. Metallization applications include nano-circuitry and automotive plating on plastic. Catalytic applications include the Heck and Suzuki reactions and a variety of other coupling reactions (hydrogenation, dehydrogenization and petroleum cracking). A common synthesis route for Pd nanoparticles is reduction of PdC12 with stannous compounds. The structure and purity of the resulting particles is critical to their performance. TEM has been used to examine PdSn nanoparticles for their compositional structure. For very small particles, EDS and EELS analyses become difficult due to the expanded excitation volume. Surface sensitive methods have utility for effective characterization of materials of this type. This work demonstrates the utility of scanning Auger analysis in characterization of particles of this type that effectively compliments TEM methods.

**Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Focus Topic**

**Room: Hall D - Session QC+AS+BI+MN-ThP**

**Fundamentals & Biological, Energy and Environmental Applications of Quartz Crystal Microbalance Poster Session**


Nano-material has grown from scientific interest to commercial products and there are more than 1600 nano-material products on the market. Among those nano-materials, single-walled carbon nanotube (SWNT) and silver ion have been shown great interest due to their extraordinary properties. Since SWNT and silver ion production capacity increases each year, its contamination to the environment water system will increase in the form of industrial waste. Moreover, toxicity assessment of those materials is required for human health and environmental issue since the toxicity of those materials has been reported. In this study, we propose the in-situ detection of SWNT and silver ion. The detection mechanism is based on the measurement of the resonance frequency shift arisen from the binding on the DNA immobilized quartz crystal microbalance. We are able to detect SWNT and silver ion less than an hour with the detection limit of 100 ng/mL of SWNT and 100 pM of silver ion, respectively. Moreover, the DNA immobilized quartz crystal microbalance enables the detection in real tap water. This work shows the potential of DNA immobilized quartz crystal microbalance as the in-situ toxic nano-material screening tool.

**QC+AS+BI+MN-ThP2 Mechanics of Multicontact Interfaces Studied with a QCM. R. König, S. Hanke, J. Vlachová, D. Johannsmann, Arne Langhoff, Clausthal University of Technology, Germany**

The contact stiffness and the contact strength at interfaces between rough surfaces are of outstanding relevance in many different fields, including mechanical engineering, bio-lubrication, and technical tribology. Individual sphere-plate contacts have been previously investigated with a QCM and it was found that the contact stiffness can be inferred from the frequency shift, where the latter is positive because contact increases the overall stiffness of the composite resonator. At elevated amplitude of oscillation, the apparent contact stiffness decreases because of partial slip. Partial slip (also: "microslip") describes the situation, where a contact partly sticks and partly slips. Sticking mostly is observed in the center. Slip is found at the edges, where the local stress is large.

The presentation describes the extension of this work to multicontact interfaces as well as the new results which were found with the single contacts. Generally speaking, multicontact interfaces differ from individual contacts by, firstly, a broad distribution of contact size and contact strength and, secondly, by an elastic coupling between neighboring load-bearing asperities.

Different materials (aluminum, PMMA) and different characteristic scales of roughness (all in the range of many microns) were studied. The focus is on polymer surfaces, which were treated with an abrasive paper. A novel geometry, where the resonator is symmetrically loaded with the same type of sample from both sides, has allowed to increase the normal force by a factor of 10, compared to previous experiments.

At small amplitudes, the frequency response of the QCM to a contact with rough PMMA surfaces is similar to the behavior observed with individual spherical contacts. There is a local resonance frequency, which can be converted to an interfacial stiffness. Interesting, the contact stiffness observed with MHz excitation was found much higher than what has been found similar samples with excitation frequencies in the kHz range.

At elevated amplitudes, the behavior is variable. Often one finds partial slip. Occasionally, however, there is a sharp increase in contact stiffness at a certain threshold in amplitude. The bandwidth goes through a maximum at that same amplitude. The behavior is reversible; the threshold is the same for decreasing and increasing amplitude ramps. We tentatively associate the increased apparent stiffness with an oscillation-induced increase in contact area.


**Scanning Probe Microscopy Focus Topic**

**Room: Hall D - Session SP+AS+EM+NS+SS-ThP**

**Scanning Probe Microscopy Poster Session**

SP+AS+EM+NS+SS-ThP2 Fabrication of Single-Walled Carbon Nanotube Probe and Processing of Single Nanometer Scale Pit with High-Aspect-Ratio of Highly Oriented Pyrolytic Graphite Using by STM. Syun Ohsuimimoto, A. Matsumuro, Aichi Institute of Technology, Japan

Our unique fabrication methods of high-aspect-ratio nanometer scale three-dimensional structures of pits, lines and convex parts using a multi-wall carbon nanotube (MWWNT) with diameter of about 50 nm as a STM probe have been developed successfully. It turned out that this method has been applicable to surfaces of various conducting materials, such as noble metal thin films, low-resistivity single crystalline silicon wafer and highly oriented pyrolytic graphite (HOPG). We also have confirmed that the physical origin of this nanometer-scale pit processing using STM must be the field evaporation mechanism by the results of TEM in-situ observations during fabrication process. In order to realize further ultra-precision three dimensional structures with high aspect ratio, it is surely required that an innovative ultimate ultra-precision processing technology needs fabrication size below several nm, i.e. single nanometer scale.

This study paid great attention to realize the ultimate processing of single nanometer scale structures using a single-wall carbon nanotube (SWNT) probe as our original STM processing. The most important problem was to overcome to much difficulty in synthesis of SWNT probes with high probability. Then, the application of mixed dispersion liquid retaining both MWWNTs and SWNTs could be devised at the process of producing SWNT probes. In this process, it was clarified that the SWNT easily attached to the point of the MWWNT, which was easily adhered to the apex of the conventional tungsten needle through the pulling method that we developed originally. The success rate for synthesis of the SWNT probes with diameter of about 2 nm and 10 nm were drastically increased up to about 10 % and 14 %, respectively. As compared with the ease where the dispersion liquid of only SWNT is used, success fabrication rate has been nearly equal to 0 %.

Single nanometer scale pits were actually fabricated on HOPG in atmosphere and room temperature condition. The SWNT probe with diameter of about 2 nm under the conditions of a bias voltage of 5 V, tunnel current of 1 nA and fabrication time of 60 s could realize a single nanometer scale pit with the diameter of 9 nm and the depth of 13 nm. The aspect ratio with SWNT probes increased up to about 5 times in the case of
Electrides are electronic materials in which excessive electrons are confined into cavities defined by the crystal structure. These excessive electrons take the place of negatively charged ions in an ionic crystal. The geometry of the cavities confining these anionic electrons determines the electronic properties of the material and provides a platform to study various aspects of 2-dimensional transport in the electron layers.

In the present work, we use an ultra-low temperature scanning tunneling microscope to investigate the local electronic structure of a cleaved surface of a Ca$_2$N single crystal. An energy gap was observed in the tunneling spectrum with a gap size of 0.4 meV. The spectra contain multiple coherence-like peaks which are equally spaced in energy, suggestive of diffusive 2-dimensional transport in the electron layers. Temperature-dependent tunneling spectroscopy measurements show a gradual suppression of the energy gap up to 2.5 K. An interesting observation is that the gap structure and the peak features do not get suppressed in the presence of a perpendicular magnetic field up to 14.5 T, suggesting if the crystal is in a superconducting state, then the critical field is extremely large compared to the transition temperature. These observations and further discussion of possible unconventional superconductivity will be discussed in this presentation.


SP+AS+EM+NS+SS-ThP3 Probing the Electronic Structure of the Layered Electrode Ca$_2$N, Jeonghoon Ha, NIST/Maryland Nano Center, Korea University of Maryland, H. Baek, NIST & Seoul National University, Republic of Korea, D. Zhang, NIST/Maryland Nano Center, University of Maryland, Y. Kim, S. Kim, J. Song, Sungkyunkwan University, Republic of Korea, Y. Kuk, Seoul National University, Republic of Korea, J.A. Stroscio, NIST

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Atom Probe Tomography Focus Topic
Room: 301 - Session AP+AS+NS+SS-FrM
Correlative Surface and Interface Analysis with APT
Moderator: Arun Devaraj, Pacific Northwest National Laboratory

8:20am AP+AS+NS+SS-FrM1 Correlative Transmission Electron Microscopy and Atom Probe Tomography of Interfaces in CdTe. David Diercks, J.J. Li, C.A. Wolden, B.P. Gorman, Colorado School of Mines

CdTe solar cells are a promising thin film technology, yet the highest reported efficiencies [1] remain well below the theoretical efficiency for such materials. For polycrystalline CdTe, interface contacts and grain boundaries along with impurities likely account for the majority of this underperformance.

Atomic scale analysis is an important feedback mechanism to relate the structure to both the device performance and the processing conditions. Through this, the atomic scale factors which improve or limit the performance can be ascertained. This then enables the development of materials and processing methods which best eliminate or mitigate the detrimental effects.

With these goals, atom probe tomography (APT) in conjunction with transmission electron microscopy (TEM) was used to study the contact interfaces and grain boundaries in CdTe devices. With the combination of time-of-flight mass spectrometry and point projection microscopy by controlled field evaporation, APT has the ability to obtain tens of ppm composition sensitivity along with near atomic-level spatial resolution. TEM provides crystallographic information along with other correlative information for guiding the reconstruction of the APT data.

It is demonstrated that the compositions measured for CdTe by APT are sensitive to the analysis conditions. Therefore, the APT analysis conditions for obtaining accurate measurements of the specimen stoichiometry were first ascertained. Following that, TEM and APT analyses of thin film devices consisting of a fluorine-doped tin oxide coated glass substrate subsequently coated with CdS, CdTe, Cu-doped ZnTe, and Au were performed. Using optimized values, APT analyses on the absorber layers and contact interfaces after different deposition and processing conditions were performed. These show significant changes in copper and sodium distributions as a result of the thermal processing.


9:00am AP+AS+NS+SS-FrM2 Atom Probe Compositional Analysis of Nanoscale Precipitates in Nb-Ti Micro-alloyed Steels. Monica Kapoor, G.B. Thompson, University of Alabama, R.M. O'Malley, Nucor Steel

Composition of complex carbide and carbo-nitride precipitates in Ti-Nb micro-alloyed 80 ksi (0.06 wt. % Nb; 0.06 wt. % Ti) and 100 ksi (0.03 wt. % Nb; 0.12 wt. % Ti) steels was studied using atom probe tomography. Fine (~2 nm) and coarse (~8 nm) NbTiC precipitates were identified in the 100 ksi steel with the Fe content decreasing with increasing precipitate size. Both steels had coarse NbTiCN precipitates (~ 80 nm) having ~7 at. % and ~30 at. % Nb in the precipitates for the 100 ksi and 80 ksi steels respectively. Star-shaped TiC precipitates and parallel rows of interphase NbTiC clusters on and near grain boundaries were also identified in the 100 ksi steel. In the 80 ksi steels, uniformly distributed disk-shaped and spherical NbTiC clusters were observed along dislocations. The composition and phase stability of these precipitates are discussed in terms of Thermo-Calc solution thermodynamic modeling.


A widely used method to immobilize nuclear wastes is fusing them into glasses. These proposed glass waste forms are multicomponent complex material with the common components of Li and B compounds. It is difficult for commonly-used surface analysis tools (e.g., X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, scanning electron microscope/energy dispersive spectroscopy (SEM/EDX), and transmission electron microscope/energy dispersive spectroscopy (TEM/EDX)) to image the distributions of ultra-light elements like Li and B with sub-micron lateral resolutions. Time-of-flight secondary ion mass spectrometry (ToF-SIMS), NanoSIMS, and atom probe topography (APT) were used to image Li and B distributions in several representative glass samples. ToF-SIMS can provide ~100 nm lateral resolutions if using Li+ and BO2− images. However, both positive ion mode and negative ion mode are used and vice versa for either unipolar ion modes. The negative ion mode can provide adequate intensity to form qualified images. NanoSIMS can provide ~100 nm lateral resolutions if using Li+ and BO2− images, while the lateral resolution of positive ion mode of NanoSIMS is poor (~400 nm). APT can provide ~2 nm lateral resolution for Li+ and B⁻ in a 3-D mode and quantification of APT is better than that of SIMS. While APT can provide much better ultimate lateral resolution than ToF-SIMS and NanoSIMS, it has three drawbacks: limited field-of-view, time-consuming sample preparation, and frequent/unpredicted sample damage during measurement. As a comparison, field-of-view of SIMS is flexible, sample preparation is simple, and little unpredicted sample damage occurs during SIMS measurement. Therefore, SIMS and APT can be regarded as complimentary techniques in nanoscale imaging of Li and B in glass samples.

9:40am AP+AS+NS+SS-FrM5 Application of (S)TEM and Related Techniques to Atom Probe Specimens. William Lefebvre, D. Hernandez-Maldonado, F. Cavalli, F. Moyer, University of Rouen, France

The geometry of atom probe tomography (APT) specimens strongly differs from standard scanning transmission electron microscopy (STEM) foils. Whereas the later are rather flat and thin, APT tips display a curved surface and a significantly larger thickness. As far as a correlative approach aims at analyzing the same specimen by STEM and APT, it is mandatory to explore the limits and advantages imposed by the particular geometry of APT specimens to STEM.

High angle annular dark field (HAADF) in STEM provides a contrast related to atomic number and to the amount of atoms in a column. A complete analysis of a high resolution HAADF STEM image requires the identification of projected column positions, the calculation of integrated HAADF intensity for each column and, eventually, the estimation of a “background level” generated by the amorphous carbon or oxide layer present on the specimen surface. Then, by of a statistical analysis [1], the possibility of atomic counting in an APT specimen can be explored. For this purpose, we propose an image processing method which provides a complete analysis of HAADF STEM images, that was applied here to APT specimens. In order to estimate the advantages and limitations of the method for such a particular specimen geometry, simulations have been applied and confronted to experimental results. Illustrations will be given for specimens before and after field evaporation in APT.


10:40am AP+AS+NS+SS-FrM6 APT Analysis of Biological Materials. Daniel Perea, J. Liu, J.A. Bartrond, N.D. Browning, J.E. Evans, Pacific Northwest National Laboratory

Biointerfaces play an essential role for the function of many biological materials and organisms. The behaviors of complex macromolecular systems at materials interfaces are important in the fields of biology, environmental biology, biotechnology, and medicine. An understanding of the chemical processes and physics, and ultimate the ability to engineer biomaterials and microorganisms with specific properties and functions, is aided by an atomic level understanding of the composition and morphology of biointerfaces. However, a great challenge exists to map the atomic composition and morphology of biointerfaces using APT, precluding a complete understanding of the structure properties relationship. At the Environmental Molecular Sciences Laboratory (EMSL), the application of APT is being developed in combination with other microscopy and spectroscopic techniques to study interfaces in biologic materials. We are developing methodologies and analyses that are allowing us to probe the ultimate limits of what APT analysis can confidently provide despite the complex thermally-assisted field evaporation behavior of soft materials. Advanced sample preparation techniques will also be discussed that further advance the application of APT into field of biology.

83 Friday Morning, November 14, 2014
Applied Surface Science
Room: 316 - Session AS+MC+SS-FrM

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

8:20am AS+MC+SS-FrM1 Vector Potential Photoelectron Microscopy, Raymond Browning, R. Browning Consultants
Vector potential photoelectron microscopy (VPPEM) is a new class of synchrotron based analytic spectromicroscopy using NEXAFS and XPS spectroscopy. To optimize the spatial resolution VPPEM images very low energy photoelectrons which poses both challenges and opportunities. At low energies the NEXAFS signals have an information depth that is similar to that from total yield absorption (TAX) measurements, while the XPS signals have a variable information depth from the universal curve at low energies. VPPEM has a very high depth of focus, and immunity to many imaging artifacts such as surface charging, and magnetic state. This makes VPPEM suitable for analyzing real world samples, and we present some results from the prototype instrument at NSLS.

8:40am AS+MC+SS-FrM2 Hydrogen and Chemical Quantification of an Organic Coating, Paul Mack, Thermo Fisher Scientific, UK
Zinc-coated steel substrates often have an additional organic coating applied, protecting the steel surface or altering its appearance for decorative reasons. X-ray Photoelectron Spectroscopy (XPS) is an analysis technique which provides chemical bonding information from the top few nanometres of a surface down to many microns in depth. It is the ideal technique, for example, for identifying the carbon functional groups in these organic coatings. XPS cannot detect hydrogen, however, but the complementary technique of Reflection Electron Energy Loss Spectroscopy (REELS) is able to both detect and quantify hydrogen. REELS can also be used to discern between aliphatic and aromatic carbon in the organic coatings. There is also a requirement for compositional profiling of these coatings, combining the excellent depth resolution and chemical specificity of XPS with some kind of ion beam sputtering. Traditional methods such as argon monomer ion profiling can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials. Numerous studies over recent years, however, has shown that argon cluster beams may be used for depth profiling while preserving chemical information during analysis of organic materials.

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

9:00am AS+MC+SS-FrM3 Mechanical Strain Induced Tunable Reflective and Conducting Silver Nanorods Embedded PDMS Film, Pratibha Goel*, J.P. Singh, Indian Institute of Technology, India
The formation of metallic films on both inorganic and organic polymeric substrate continues to be of substantial interest because of various applications.1,2 Polymeric supports offer the obvious advantages in weight, flexibility, elasticity, and fragile relative to inorganic support such as glasses, ceramics, or native metal. Silver is a metal of choice as a reflecting material because of its high reflectance coefficient (0.93). Silver also has the highest electrical conductivity of all metals at 6.3 x 10^4 (Ωm)^{-1}. However, there are disadvantages of using silver as the reflecting metal. Firstly, silver is a relatively soft metal so that the face of a mirror needs to be carefully protected from mechanical abrasion. Secondly, silver tends to tarnish which diminishes its reflectivity. (Ambient sulfur-containing compounds are a particular problem.) Thirdly, and perhaps the most important, silver(0), as a more passive metal, does not interact strongly with organic functionalities, which means that adhesion of a silver layer on a polymer surface can be a substantial problem.

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

References:

9:40am AS+MC+SS-FrM5 Surface Analysis of Electronic Materials, L.I. Opila, Kevin Jones, J. Church, University of Delaware, R. Gupta, V. Pallemon, B. Lejevre, Air Liquide, X. Lin, University of Delaware
Surface analysts at the University of Delaware have used a variety of surface analytical techniques to analyze films for electronic materials applications. These films were deposited by a variety of techniques including plasma enhanced chemical vapor deposition, molecular organic chemical vapor deposition and atomic layer deposition using precursors synthesized at Air Liquide. Methods of analysis include x-ray photoelectron spectroscopy, scanning Auger electron spectroscopy, time-of-flight secondary ion spectrometry, nano-indentation and synchrotron-based hard x-ray analysis. The advantages of each technique for particular analyses will be discussed.

10:40am AS+MC+SS-FrM8 Lewis Base Sites on the Nitrogen-Doped Graphite Surfaces Probed by CO2 Adsorption, Takahiro Kondo, R. Shibuya, S. Morohoshi, D. Guo, J. Nakamura, University of Tsukuba, Japan
Carbon materials have been reported to exhibit unique adsorption property and catalytic activity when they have received specific treatments such as nitrogen doping. For example nitrogen-doped graphite has been reported to show the superior catalytic activity for the oxygen reduction reaction (ORR) in fuel cell [1]. To understand the origin of such specific properties at the atomic scale, we are now trying to examine the relationship among the localized electronic states of the carbon atoms, the adsorption property of the molecule, and the catalytic activity towards ORR by using model catalyst of graphite with surface science techniques. Previously, we have reported [2] that the carbon atoms around a pyridinic-nitrogen (N having two N-C bonds) in a highly oriented pyrolytic graphite (HOPG) have occupied localized states near the Fermi level [2]. We consider that such carbon atoms may act as Lewis base sites [2] and may relate to the ORR activity. In this work, we have examined this hypothesis by observing the carbon dioxide adsorption property with temperature programmed desorption (TPD), ORR catalytic activity measurement, and X-ray photoelectron spectroscopy (XPS).

To prepare the pyridinic-nitrogen-doped graphite (p-N-HOPG) as the model catalyst, we have firstly cleaved the HOPG at atmosphere and then bombarded it by the nitrogen ion through Ni patterned mask to make edges with N-termination. After the bombardment, the sample was put into HNO3 solution for 72 hours to remove Ni impurity. The sample was annealed at 900 K for 2 hours in ultrahigh vacuum. XPS spectrum shows that the nitrogen atoms in the prepared sample consists of over 60 % pyridinic-nitrogen, suggesting that nitrogen atoms are dominantly doped at the edges.

In TPD measurements, CO2 desorption peak was observed at around 370 K from p-N-HOPG after the 1000 L CO2 exposure at 300 K, while no CO2 desorption peak was observed from clean HOPG. These results indicate that Lewis base sites are formed on p-N-HOPG. The same CO2-TPD results were reproducibly observed by sequential 4 time measurements. This means Lewis base sites on p-N-HOPG does not change by the CO2 adsorption and desorption. Details of ORR catalytic property on p-N-HOPG, its relationship with ORR activity and the influence of nitrogen configuration on the carbon atoms in p-N-HOPG will be discussed.


Graphene has brought spintronic devices that depend on the ability to transport spin much closer to realization. Graphene’s high carrier mobility and low spin-orbit scattering allow for efficient transport.
spin transport, which has been demonstrated by several publications over useful length scales [1,2].

Further progress toward more sophisticated spintronic devices requires controllable manipulation of spin polarized charge carriers. A graphene Spin-Field Effect Transistor has been proposed by Semenov et al [3] that manipulates the spin of charge carriers in a graphene channel by an exchange interaction with a hypothetical ferromagnetic dielectric. As an alternative that also adds functionality, we have identified Cr2O3 as a material whose magnetoelectric properties would enable voltage controlled switching of the exchange interaction. The Magnetoelectric properties of Cr2O3 have been extensively studied [4], including recent reports of a robust electrically switched magnetic surface state [5,6].

We used pulsed laser deposition to grow thin Cr2O3 films directly on HOPG. AFM shows a smooth Cr2O3 film with the hopp topography preserved. X-Ray Diffraction shows that the film has a (0001) texture for films grown at 300 - 650°C, which is the strongest orientation of the magnetoelectric effect. The Magnetic polarization of the film can be aligned by magnetoelectric annealing and locally switched with conducting AFM, the effects of both are observed by magnetic force microscopy.


Energy loss measurements of highly charged ions in the low kinetic energy regime have been made using as-grown SiO2 (170nm) targets. Highly charged Ar⁹⁺ ions (Q=4, 8 and 11) with a kinetic energy of 1 keV were used to produce electronic excitations in the oxides. The irradiated regions of the oxide were then encapsulated under a top metallic contact to form metal-oxide-semiconductor (MOS) devices. The devices were probed with capacitance-voltage (C-V) measurements and the extracted flatband voltages from the C-V curves were correlated with ion energy (kinetic and potential).

The C-V results for highly charged ion experiments reveal that the changes in the flatband voltage and slope for implanted devices relative to the pristine devices can be used to delineate effects due to implanted ions only and ion induced damage. The results confirm that dose as well as and charge-dependent effects can be recorded for irradiation of oxides using this method. In particular, the results as a function of charge state indicate that there is a significant enhancement in the induced flatband voltage shift as the charge state of the beam is increased. This was quantified by measuring the flatband voltage shift across multiple ion doses for fixed incident charge state. The results as a function of the charge state of the beam are consistent with some theoretical predictions.

Spectroscopic Ellipsometry Focus Topic Room: 304 - Session EL+AS+BI+EM+SS-FrM

Application of SE for the Characterization of Organic and Biological Materials

Moderator: Tino Hofmann, University of Nebraska-Lincoln

8:20am EL+AS+BI+EM+SS-FrM1 Multimodal Optical and Mass Spectrometric Imaging of Cells and Tissues. DaeWon Moon, DGIST, Republic of Korea

Understanding interfacial phenomena has been one of the main research issues not only in semiconductors but also in life sciences. We have been trying to use the atomic scale surface and interface analysis challenges from semiconductor industries and furthermore to extend the application scope to biomaterial areas. Optical imaging has been widely used and successfully used for biomedical imaging but complementary mass spectrometric imaging can provide more detailed molecular specific information.

In this presentation, I report our recent activities of multimodal nanobio imaging of cardiovascular cells and tissues, firstly, in atherosclerotic plaque imaging using coherent anti-stokes ram scatter imaging (CARS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS), multimodal CARS & SIMS analysis showed that increased cholesterol palmitate may contribute to the formation of a necrotic core by increasing cell death. Secondly, surface plasmon resonance imaging ellipsometry (SPRIE) was developed for cell biointerfacing imaging of cell adhesion, migration, and infiltration dynamics for HUVEC, CASMC, and T cells. SPRIE images were validated with confocal fluorescence microscopy. Collagen fibrils are widely used as cell adhesion substrates. Changes of surface composition and elastic modulus of collagen fibrils after thermal and acidic treatment were investigated by TOF-SIMS and non-contact force microscopy. Multimodal SPRIE & TOF-SIMS imaging would be a useful methodology for understanding cell-substrate interactions in tissue engineering.

In conclusions, multimodal optical and mass spectrometric imaging provides overall structural and morphological information with complementary molecular specific information, which can be a useful methodology for biomedical studies. Future challenges in optical and mass spectrometric imaging for new biomedical applications will be discussed regarding to in-vivo imaging.


Spectral Mueller matrices are very rich in information about physical properties of a sample. We have recently shown that polarizing properties like ellificticity and degree of polarization, can be extracted from a Mueller matrix measured on a beetle cuticle (exoskeleton). Mueller matrices can also be used in regression analysis to model nanostructures in cuticles. Here we present the use of sum decomposition of Mueller matrices from these depolarizing biological reflectors to explore the fundamental character of these reflectors. The objective is to decompose a Mueller matrix into well-defined ideal non-depolarizing matrices corresponding to mirrors, circular polarizers, halfwave retarders etc. Generally it is possible to decompose a measured depolarizing Mueller matrix M into four (or fewer) non-depolarizing matrices according to $M = a M_1 + b M_2 + M_3 + M_4$, where $a$, $b$, $γ$, and $δ$ are eigenvalues of the covariance matrix of M. Two strategies for decomposition will be discussed. A Coande decomposition will provide the eigenvalues and also the M’s although the latter will contain severe noise in some spectral regions. However, a major advantage with the Coande decomposition is that the number of nonzero eigenvalues is directly obtained, i.e. the number of contributing M matrices. In an alternative decomposition, the M’s are assumed and the eigenvalues are found by regression analysis based on $M$. In the case with two non-zero eigenvalues we define a model Mueller matrix $M_{0} = a M_1 + b M_2$ with $a + b = 1$. With $\alpha$ as adjustable parameter, the Frobenius norm $||M - M_{0}||$ is minimized for each wavelength in the spectral range of M. For more complex structures, the regression can be extended by adding more matrices up to a total of four. Advantages with a regression approach are its simplicity and stability compared to a Coande decomposition. The Mueller-matrix spectra of beetle cuticles are recorded with a dual rotating compensator ellipsometer in the spectral range 400 – 900 nm at angles of incidence in the range 20 - 75°. The application of decomposition on biological reflectors is demonstrated on M measured on the beetle Cetonia aurata, which represents a narrow-band chiral Bragg reflector with two non-zero eigenvalues. A decomposition in an ideal mirror and a circular polarizer is feasible. In another example, the broad-band and gold-colored beetle Chrysisina...
argentoela, we show that more than two eigenvalues can be nonzero, especially at oblique incidence, and additional matrices are involved.

Membrane structures consist of thin continuous layers deposited on porous ceramic or polymer supports. We have been developing inorganic and hybrid membranes for various applications that include gas separation (e.g., post-combustion CO2 capture), water purification, Solid Oxide Fuel Cells (SOFC) and sensors. Spectroscopic Ellipsometry (SE) is a major non-destructive characterization tool, which can be used to obtain the thickness (typical range 50 nm...2 μm) and complex refractive index (n,k) of the supported membrane layers. This information, in turn, is used to obtain information about membrane composition, porosity and gas or water sorption. The characterization of fully-ceramic structures on optically smooth or porous α-alumina surfaces (roughness ~25 nm, higher than most typical SE applications) has been employed by our group for several years. Recently we have expanded the use of SE to characterization of multi-layered membranes, and of inorganic or polymer layers on polymer supports, on coarser α-alumina surfaces, and on ceramic tubes. Examples are γ- and α-alumina on polyethersulfone (PES) and poly-sulfone (PES), C60,Cd0.62O(1.8) on tubular α-alumina, and successive layers of an amorphous microporous silica and polydimethylsiloxane (PDMS) on mesoporous intermediate layers. We have achieved signal detection and interpretation to acquire meaningful results, even in multi-layered structures and in cases with substantial interfacial surface roughness, or curvature. Overall, the application of SE, including non-destructive characterization at intermediate stages between deposition and processing steps, can significantly facilitate the design of gas separation membrane structures that combine organic and polymer layers.

Spectroscopic ellipsometry (SE) is a powerful tool for studying thin films, including the thickness and dielectric function, the latter being closely related to important properties such as composition, phase, grain size, porosity, and stress. The sub-nanometer sensitivity of SE is best exploited if the detector and the extension of the light source, the extension of the detector and the extension of the illuminated sample area (especially its depth) are reducing the value above. The measured intensity at the detector is described by the correlation which exists between these two orthogonal directions. Furthermore the extension of the light source, the extension of the detector and the extension of the illuminated sample area (especially its depth) are reducing the value above. The measured intensity at the detector is described by the correlation which exists between these two orthogonal directions.

Depolarization: The end point of the field of unpolarized light may be assumed to move quite irregularly, and the light shows no preferential directional properties when resolved in arbitrary orthogonal directions normal to the direction of propagation. Depolarization is mathematically described by the correlation which exists between these two orthogonal directions. Furthermore the extension of the light source, the extension of the detector and the extension of the illuminated sample area (especially its depth) are reducing the value above. The measured intensity at the detector is described by the correlation which exists between these two orthogonal directions.

In this work, an improved SE methodology has been developed, tested, and applied to study thin films with significant surface non-idealities. The investigated materials include Cu(InGa)Se2, Zn(O,S), Cu2ZnSnS4, and Cu2SnS3 deposited on transparent substrates by co-evaporation, sputtering, or chemical bath deposition. The film thicknesses in this study range from ~20 to 4000 nm, with potential applicability of the methodology over an even wider range. The key component of the SE methodology is integration of through-the-substrate (TS) SE with standard film-side (FS) SE. The following successes have been demonstrated.

1. When the surface non-ideality is predominantly roughness within the EMA applicability, two-side (FS+TS) SE can minimize dielectric function distortion caused by the EMA assumptions.

2. When the surface non-ideality is outside the EMA applicability and traditional SE methodology becomes unreliable, accurate results can be obtained using the FS+TS SE methodology, in which the dielectric functions of the surface and bulk layers can be allowed to vary wavelength by wavelength independently. Most thin films of this study fall into this category.

3. When the surface is macroscopically rough and scatters light, films can be grown intentionally thick and hence rough enough to suppress specular reflection from the surface. In this case, through-the-substrate SE alone can be used to extract the bulk film dielectric function.

An important criterion for evaluating SE analysis on semiconductor films is that the ε2 spectrum should be flat and essentially zero below the band gap. It is demonstrated that the dielectric functions obtained through the above SE methodology either satisfy or better satisfy this criterion compared to previous studies. The limitations of the SE methodology will also be discussed.

Spectroscopic Ellipsometry (SE) is a powerful tool for studying thin films with significant surface non-idealities. The photon energy range of strong absorption is related to important properties such as composition, phase, grain size, or curvature. Overall, the application of SE, including non-destructive characterization at intermediate stages between deposition and processing steps, can significantly facilitate the design of gas separation membrane structures that combine organic and polymer layers.
Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+AS+BI+EM+NS+SE+SS-FrM
Probe-Sample Interactions and Emerging Instrument Formats
Moderator: Carl Verrettie, Jr., University at Albany-SUNY
8:40am SP+AS+BI+EM+NS+SE+SS-FrM2 2013 ASD Student Award Talk: New Insights into Nanoscale Adhesion from In Situ TEM Studies, Tevis Jacobs, J.A. Lefever, University of Pennsylvania, J. Liu, University of Wisconsin-Madison, D.S. Grierson, SysteMECH LLC, K.E. Ryan, P.L. Keating, J.A. Harrison, United States Naval Academy, K.T. Turner, R.W. Caprichick, University of Pennsylvania
A fundamental understanding of adhesion is important for applications at all length scales, particularly critical for nanoscale devices and applications due to their high surface-to-volume ratio. Advancements in studying such tribological phenomena are typically hindered by the inaccessibility of the sliding interface. We will present nanoscale adhesion measurements conducted inside of a transmission electron microscope (TEM), using a modified in situ nanoindentation apparatus that makes contact with atomic force microscope (AFM) cantilever tips. This tool provides new opportunities to observe, identify, and quantify tribological processes with unprecedented access and resolution. First, using ultrastrong carbon-based tip materials, we find that roughness of tips can greatly reduce the pull off force and lead to severe underestimation of the work of adhesion [1]. Furthermore, we have quantified adhesion by making and breaking contact between nanoscale silicon asperities and a flat diamond substrate. The pull-off force and the pull-off area were found to be consistent with sub-nanometer and sub-nanowatt resolution, respectively. The shape of the Si asperity is determined with sub-nanometer resolution immediately before and after contact to verify that elastic conditions were maintained. From this, we independently determine the work of adhesion and range of adhesion. The results show that accounting for roughness has a strong effect on both parameters. These two results demonstrate the importance of applying in situ approaches to studies of adhesion. ---- 1. Jacobs, T.D.B., Ryan, K.E., Keating, P.L., Grierson, D.S., Lefever, J.A., Turner, K.T., Harrison, J.A. and Caprichick, R.W. The Effect of Atomic-Scale Roughness on the Adhesion of Nanoscale Asperities: A Combined Simulation and Experimental Investigation. Tribol. Lett. 50, 81-93 (2013).

9:40am SP+AS+BI+EM+NS+SE+SS-FrM5 Nanoscale Mapping of the W/Si(001) Schottky Barrier using Ballistic Electron Emission Microscopy, Christopher Durcan, University of Albany-SUNY, V.P. LaBella, University at Albany-SUNY
The W/Si(001) Schottky barrier was spatially mapped using ballistic electron emission microscopy (BEEM) and ballistic hole emission microscopy (BHEM) using high resistivity n-type and p-type silicon substrates. A thin tungsten silicide is observed upon deposition utilizing the Adhesion of Nanoscale Asperities: A Combined Simulation and Experimental Investigation. Tribol. Lett. 50, 81-93 (2013). The tunneling spectra of YPdBi show two different superconducting gaps of 0.36 meV and 0.16 meV depending on the measurement location. The variation in gaps might originate from inhomogeneity in the crystal. The superconducting gap of 0.36 meV is completely suppressed above a critical magnetic field of 2=5 T, in agreement with bulk transport measurements. A superconducting gap of 0.21 meV and an upper critical field of 1.25 T were measured in a circular superconducting domain of diameter ~180 nm in YPbBi. Sequential addition of single layers to the superconducting YPbBi domain could be observed with increasing magnetic field, with vortices occupying the perimeter of the island. These observations will be discussed in terms of island confinement and pairing symmetry of YPbBi.


10:40am SP+AS+BI+EM+NS+SE+SS-FrM8 Multimodal Intermittent Contact Atomic Force Microscopy, Topographical Imaging, Compositional Mapping, Subsurface Visualization and Beyond, Santiago Solares, George Washington University
Multifrequency atomic force microscopy (AFM) refers to a family of techniques that involve excitation of the cantilever probe at more than one frequency [R. Garcia and E.T. Herruzo, Nature Nanotechnology 7, 217 (2012)]. This can be carried out in a sequential manner, varying the excitation frequency over time, as in chirp band excitation methods, or simultaneously supplying drive signals containing more than one frequency to the cantilever shaker. The latter mode of operation commonly involves the simultaneous excitation of more than one cantilever eigenmode, such that each eigenmode is used to carry out different functions. For example, in a recently developed trimodal imaging scheme for soft sample characterization [D. Ebeling, B. Eslami and S.D. Solares, ACS Nano, 7, 10387 (2013)], the fundamental eigenmode is used for topographical acquisition, as in standard tapping-mode AFM, while the two higher eigenmodes are used for compositional mapping and subsurface visualization, respectively. This talk presents experimental and computational results for validated multimodal imaging schemes involving one to three eigenmodes, and discusses the expected benefits and complexities of including more than three eigenmodes.

Thin Film
Room: 307 - Session TF+AS+FrM
Thin Film Characterization
Moderator: Mark Davidson, University of Florida
8:20am TF+AS+FrM1 Stability of Platinum Silicide Thin Films above 1000°C, Robert Fryer, R.W. Meulenberg, G.P. Bernhardt, R.J. Lad, University of Maine
Stable, electrically conductive thin films are needed as components for sensors and actuators operating in harsh environments at temperatures above 1000°C, such as those found in turbine engines, power plants, and high temperature materials manufacturing. The Pt-Si thin film system has been extensively studied in the microelectronics industry but the focus has been on film characteristics below 800°C. In this work, Pt-Si films were grown at varying compositions and deposition temperatures on sapphire and fused silica substrates by electron-beam evaporation of Pt and Si sources in ultra-high vacuum (~1x10^-10 Torr); the chemical and thermal stability of the Pt-Si films, both in air and in vacuum, at temperatures between 1000-1200°C were studied. X-ray diffraction (XRD) of as-deposited films indicates the formation of a polycrystalline tetragonal-PtSi phase for Pt-rich film compositions, an orthorhombic-PtSi phase near the PtSi composition, and an amorphous film for Si-rich film compositions. The electrical conductivities of these films, measured by a 4-point probe, are in the range of 1x10^3 to 5x10^4 S/m, with the conductivity decreasing at higher Si content. Annealing in vacuum at 1000°C causes grain growth and a marked increase in film conductivity. During annealing in air at 1000°C, film oxidation occurs leading to the formation of Pt-oxide phases coinciding with the Pt-Si phases, but only a ~3-fold decrease in film conductivities. After air anneals at 1200°C, the Pt-Si films become insulating due to morphological roughening and formation of highly faceted Pt (111) and (200) nanocrystallites coexisting in a SiO2 matrix. Scanning electron microscopy (SEM) revealed that the use of a 50 nm capping layer of amorphous Al2O3, grown by atomic layer deposition (ALD) on top of the
Pt-Si films, helps retard oxidation thereby preserving film conductivities in the $10^{-10}$ S/m range and leading to greater film stability as a function of annealing time at 1000°C in air.

8:40am TF+AS-FrM2 Bulge Testing for Mechanical Characterization of sp$^3$/sp$^2$ Carbon Thin Films, Joseph Rowley, R.C. Davis, R.R. Vanfleet, N. Boyer, Brigham Young University; S. Liddiard, M. Harker, Moxtek, Inc.; L. Pei, Brigham Young University

Bulge testing is a technique employed to measure material properties of thin films. Pressurized gas is applied to one side of a film and its subsequent deflection measured. In many cases, thin films are fragile and therefore difficult to handle. Bulge testing has the advantage of requiring much less handling than other methods, resulting in fewer samples lost to error or accident. Carbon membranes have a wide range of characteristics, depending on their bonding and nano-structure. They can have very desirable properties such as: being chemically inert, high wear resistance and high fracture, and both hardness and strength. In this work, reactively sputtered sp$^2$ carbon, diamondlike carbon from a pulsed laser deposition process, and a carbon nanotube reinforced polymer were characterized. PELLS and Raman Spectroscopy were used to determine sp$^3$/sp$^2$ ratios and density, CHN testing was used to determine hydrogen content, measuring the resonant frequency was a measure to check stiffness, and bulge testing was used to obtain the Young's Modulus and tensile strength.

9:00am TF+AS-FrM3 Time Dependent Dielectric Breakdown Measurements of Porous Organosilicate Glass using Mercury and Solid Metal Probes, Dongfei Pei, University of Wisconsin-Madison; M.T. Nichols, Applied Materials; S.W. King, J.M. Clarke, Intel Corporation; Y. Nishi, Stanford University; J.L. Shohet, University of Wisconsin-Madison

Time-dependent dielectric breakdown (TDBB) is a major concern for low-k organosilicate (SiCOH) dielectrics. To examine the effect of plasma exposure on TDBB degradation, both the time-to-failure (TTF) and charge-to-failure (CTF) measurements [1] were made on porous SiCOH before and after exposure to Ar plasma. Significant discrepancies between mercury and solid-metal probes are observed. With XPS measurement data, a significant amount of mercury was found to have drifted into the porous SiCOH film. This implies that the electrical measurement of porous low-k material under mercury probe may be inaccurate due to this mercury drift effect.

This work was supported by the Semiconductor Research Corporation under Contract 2012-KJ-2359 and by the National Science Foundation.


9:20am TF+AS-FrM4 The Equivalent Width as a Figure of Merit for XPS Narrow Scans, Matthew Linford, B. Singh, Brigham Young University; J. Terry, Illinois Institute of Technology

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analytical tool that provides information about the near surface regions of materials. In particular, chemical state information is often obtained from peak fitting XPS narrow scans. And while indispensable for XPS data analysis, peak fitting can be a fairly subjective exercise. Herein we introduce the use of the equivalent width (EW) as an additional and less subjective figure of merit for XPS narrow scans. The EWPS is simply defined as the area of a narrow scan divided by the height of the maximum of its peak envelope. To limit any ambiguity in EWPS for a series of spectra, we may also list the peak position of the maximum of the envelope (PEmax). We provide and discuss four examples that demonstrate the use of these parameters including (i) four C 1s narrow scans of ozone-treated carbon nanotubes (EWPS ~ 2.11 – 2.16 eV for a Shirley background, and up to 2.88 eV for no background, PEps ~ 284.4 – 284.5 eV), (ii) a series of silicon wafers with different oxide thicknesses (EWPS ~ 1.5 – 2.8 eV, PEps ~ 99 – 103 eV), (iii) hydrogen-terminated silicon before and after derivatization with pentyl groups, and after annealing of the pentyl-modified material (EWPS ~ 0.7 – 1.0 eV, PEps ~ 259 – 261 eV), and (iv) five C 1s narrow scans of nanodiamond samples, where three of the spectra showed charging (EWPS ~ 2.6 – 4.9 eV, PEps ~ 272.7 – 293.9 eV). In this final example, EWPS was plotted against PEps to identify the region corresponding to the materials that showed the least charging. EWPS and PEps appear to correlate with the expected chemistries of all the systems studied. We calculate EWPS using a Shirley baseline and with no baseline at all. In setting the baseline limits for EWPS, we consider the derivative of C 1s narrow scans. We also show the application of EWPS to single, fitted components within a narrow scan. Other width functions are also discussed.

10:40am TF+AS-FrM8 Low Energy Ion Scattering Data Analysis for Ultra Thin Films using TRBS, Thomas Grehl, P. Brüner, ION-TOF GmbH, Germany; B. Detlefs, E. Nolot, H. Grampeix, CEA-LETI, France; E. Steinbauer, P. Bauer, Johannes Kepler University, Austria; H.H. Brongersma, ION-TOF GmbH, Germany

Low Energy Ion Scattering (LEIS) is well known for its extreme surface sensitivity allowing elements and interface characterization of the outermost atomic layer. This makes it a valuable tool for thin film analysis, e.g. to gain insights to the early stages of film growth or determine film closure. Also contamination analysis can be performed, again making use of the high surface sensitivity to assess the surface composition as the basis for subsequent deposition steps.

In addition, distinct information about sub-surface layers is obtained in a non-destructive way, giving information about the depth distribution of elements up to 10 nm. Although the mechanism for this in-depth signal is well understood, a model for the quantification of the data needs to be established.

One way of modeling the data is demonstrated using TRBS [1], a specialized version of TRIM [2] which was optimized for simulating ion scattering. Combining the TRBS data for backscattering of primary ions and an empirical model for the energy dependent reionization probability gives promising results. By fitting the simulation to the measured data conclusions about film composition, thickness and interface quality can be drawn.

This approach will be demonstrated using different thin film examples. One of the sample sets consisting of HfO$_2$/AlO$_x$ stacks also characterized by AR-XPS, XRR and GIXRF will be discussed in detail. We will show the possibility to determine film thickness variations in the Å range. These measurements can be performed in a few minutes without destroying the sample by sputtering. At the same time, the composition of the outer atomic layer is detected, making the approach well suited for routine analysis of films during or after deposition.


Research in organic electronics shall open up alleys for many of its promising applications, including promising applications, including: light emitting diodes, photovoltaics, transistors, biosensors and photonic devices. Despite of the diversity of device functionalities, all these applications are based on thin films of organic materials and in each case their performance is critically dependent upon the precise arrangement and packing structure of the organic molecules in thin films. Our research focuses on this fundamental issue, seeking to better understand the relationships between device performance and thin film morphology of organic semiconductors on the molecular scale [1,2].

A set of 6,13-Bis(triethylsilyl)ethylpentacene (TES-PEN) samples has been prepared on a silicon substrate by using a well controlled printing technique [2]. Different substrate shift speeds were used to modify the layer thickness and the crystallinity.

All X-ray based measurements were carried out at the plane grating monochromator PGM beamline for undulator radiation in the laboratory of the Physikalisch-Technische Bundesanstalt (PTB) at BESSY II, providing tunable radiation of both high photon flux and high spectral purity in the soft x-ray range [3]. Different kinds of X-ray spectrometry (XRS) analyses were employed to determine the chemical binding state, elemental distribution depending on the depth, and lateral mass deposition.

To analyze the chemical binding state of the molecules, the method Near-Edge X-ray Absorption Fine Structure spectroscopy (NEXAFS) in fluorescence mode has been employed. Varying the angle of incidence in the fluorescence mode the information depth can be tuned to a pre-selectable depth of interest. In addition, the mean penetration depth at large angles of incidence is high enough to analyze even thicker layers of up to a few hundreds of nanometers as is often the case for complex organic materials. For an analysis of the molecular orientation, the angle between the electric field vector and predominant direction of the molecules has to be varied.

Initial measurement sequences exhibit the potential of this X-ray spectrometry method to significantly contribute to the quantitative analysis of organic materials in thin films. In particular, polarization dependent NEXAFS offers a clear discrimination capability for the orientation of the molecules.

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