Biomaterial Interfaces
Room: 317 - Session BI+AS-MoM

Biomolecules & Biomaterials Interfaces
Moderator: Ilya Reviakine, CIC biomaGUNE

8:40am **BI+AS-MoM2 Deposition of Porous Polyparylene Layers with Even Thickness in Narrow Tubes**, ***Gerhard Franz***, *H. Heidari*, Munich University of Applied Sciences, Germany

To coat a thin hollow tube with an equally thick layer along the whole length, is one of the most challenging issues of surface refinement. Even for long mean free paths and large diffusion lengths, a drop in thickness is common, which is simply caused by the abstraction of deposited molecules, which cannot walk randomly any longer. To overcome these inherent spatial inhomogeneities, we made use of the mechanism of the temperature-dependent surface polymerization, which is manifested in the occurence of a "ceiling temperature". Negatively turned, no deposition is possible beyond this temperature. Positively spoken, the spatially inhomogeneous deposition rate along a tube can be equalized with a counteracting temperature 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" in inner diameter to be coated with a layer of even thickness. The most prominent application is 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 patent-pending procedure [1]. These silver rings act as antibacterial means to combat infections and induced incrustations in the urological area. To prolong the lifetime of the silver depot, it has to be protected with a porous human compatible top layer. We chose FDA approved polyparylene with thicknesses between 100 and 400 nm to ensure a long-term antibacterial activity, which should be kept above threshold level by a safety factor of 2 [2,3]. First results for the CVD of polyparylene are presented and are discussed and modeled with COMSOL in terms of diffusion laws with an abstraction reaction of 1st 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, 01801 (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. Baimpos, B.R. Shrestha,* ***Markus Valtiner***, Max Planck Institut fur Eisenforschung GmbH, Germany

Unraveling the complexities of the macroscopic world based on molecular level details 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 non-equilibrium single molecule force spectroscopy (SM-AFM). 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 bonds at an interface and we measure molecular acid-amine 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 calculated using JE converges rapidly to 10.7 ± 1.1 kT. This is essentially 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, the developed approach provides a strategy for molecular design of novel functional materials through predicting of large-scale properties such as adhesion or cell-substrate interactions based on single molecule or simulation experiments.

9:20am **BI+AS-MoM4 Fabrication of ssDNA Monolayers, Custom Designed ssDNA Arrays and Brush Patterns in Biorepulsive Templates by Promoted Exchange Reaction**, *M.N. Khan,* University of Heidelberg, Germany, *V. Tjong, A. Chilkoti,* Duke University, ***Michael Zharnikov***, 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 alkanethiols (OEG-AT) in a broad range of compositions as well as ssDNA/OEG-AT patterns of desired shape embedded into a biorepulsive background. The procedure involves two steps. First, a OEG-AT monolayer on a solid support is exposed to electrons or UV light in either homogeneous or lithographic fashion. Second, the promoted (by the irradiation in the first step) exchange reaction between the damaged OEG-AT species in the film and ssDNA substituents 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 electron or UV dose in almost entire composition 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. Boudjabi, D. Covelli, M. Keramane, E. Luckham,* ***John Brennan***, McMaster University, Canada **INVITED**

This presentation will highlight recent work in the area of high throughput screening of biologically modified surfaces for production of biosensors, protein and cell microarrays, and non-fouling surfaces. Using robotic material synthesis and assay systems and a combination of contact and noncontact microarray printing, we have produced several libraries of biomaterials with a wide range of chemical compositions based on acrylate, silicone and silica-based polymers. Using silica-based materials as an example, the presentation will show the workflow utilized to develop new bioactive polymer materials for generation of bioactive and stealth materials 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 non-specific 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 the body's metabolic regulation and bone building, as well as being used as a biochemical marker 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 Ca^{2+} 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 silica and HAP surfaces. Similar amounts (3-4 atomic % N) of OC and dOC were adsorbed onto the silica surface. Higher amounts adsorbed on the HAP surface (~5 atomic % N for dOC and ~8 atomic % N 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

(~x10) when the proteins were adsorbed onto silica. Since in the native OC structure the cysteines 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 above 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 absorbed 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 Baio***, Oregon State University, *D. Schach,* University of Chicago, *M. Bonn, T. Weidner*, Max Planck Institute for Polymer Research, Germany

GALA peptides (WEAALAEALAEALAEHLAEALAEALEALAA) 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 pK_a 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 Polydopamine Modification Using Small Molecule Thiols and Dithiols: Problems and Solutions for Creating Protein Resistant Coatings**, ***Marlon Walker***, *A. Vaish, D. Vanderah*, National Institute of Standards and Technology (NIST)

Polydopamine (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**, ***Tiana Shaw***, *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 if often used in pretargeting strategies for cancer treatment. In most cases a probe molecule (antibody) is connected to a marker molecule (fluorophore or nanoparticle) through the biotin-avidin bridge. Biotinylated nanoparticles can play a role in improving this interaction and creating an electronic or optical detection method. Polyaniline is a polymer which can be easily functionalized to be specific for various biomolecules and has ideal sensor characteristics. In this study we will design a process to functionalize polyaniline with biotin to create a biotin-avidin biosensor. We began with 2-acetamidophenol which is a hydroxyl substituted aniline monomer. This monomer undergoes polymerization to yield 2-hydroxy polyaniline. The polymer's hydroxyl group was functionalized by Steglich esterification which refluxes a carboxylic acid with an alcohol. This esterification drives the reaction and dehydrates the products shifting the equilibrium towards the product. In this reaction DCC (dicyclohexylcarbodiimide) activates the carboxylic acid of biotin to further reaction and DMAP (4-dimethlyaminopyridine) 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. Florescence emission studies were also carried out with the avidin protein.

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

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

Moderator: Ian Gilmore, National Physical Laboratory, Michaeleen Pacholski, The Dow Chemical Company

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

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

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

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

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

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

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

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

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

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

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

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

References:

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

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

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

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

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

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

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

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

References:

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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**, ***Erinn 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 Al_2O_3 nanocoatings showed enhanced IL-1β secretion 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)-b 1 and CXCL10, 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 the number of ALD cycles, as observed by TEM. Thicker coatings inhibited MWCNT aggregation, and sonication allowed us to induce fiber fragmentation. 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 toxicology 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. Monodispersed 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 US imaging performance in order to detect 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 very bright chromophores 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 polymer – QD activated intermediate has increased 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 un-labeled proteins with a better detection limit than any 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 gold 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 mercaptoethylamine in ethanol in a rapid process. 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), it 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 yielded the largest shifts. Strong resonant coupling was 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 Nanoparticles in Biological Media**, *P. Munusamy, J.N. Smith, C. Liu, C.-M. Wang,* Pacific Northwest National Laboratory*, S. Chen,* 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 wide-spread use of silver nanoparticles in consumer products raises questions of environmental impact and toxicity. Because both silver particles, 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 nanoparticles produced by different synthesis routes can have significantly 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 during *in-vitro* studies. Silver particles with gold cores had 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 time variation of particle size 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 or 110 nm particles. The dissolution of silver nanoparticles was also found to be enhanced by 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 silver nanoparticles 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 NIEHS 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 Belsey****, 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 farther 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 for dealing with aggregated samples, but XPS is, while XPS measurements of organic nanoparticles are challenging and liquid based techniques may be preferred.

4:40pm **BI+AS+NS-MoA9 Development of Nanofibrous Meshes as Smart Dressings for Chronic Wound Care**, ***Martina Abrigo****, P. Kingshott, S.L. McArthur*, Swinburne University of Technology, Australia

Diabetic, pressure, venous and arterial ulcers are a large social, economic and healthcare burden. These chronic non-healing wounds show delayed and incomplete healing processes exposing patients to high risk of infection. The design of wound dressings that combine the necessary morphological and physical requirements for wound healing with the value-added capability to address optimal cell responses and impair bacterial proliferation represents a major challenge in chronic wound care. Polymeric nanofibrous meshes fabricated through the electrospinning process are promising candidates as wound dressings due to their high surface area, micro-porosity and non-woven structure. In this study, the parameters of the electrospinning process (such as spinning rate and electric field intensity) were optimized to fabricate nanofibrous membrane in Polystyrene (M.W. 250.000). The morphological properties of the electrospun meshes were analysed by bright microscopy, three-dimensional optical profiler, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). Electrospun materials have been used as scaffolds for tissue engineering for a number of years, but there is surprisingly little literature on the interactions of fibres with bacteria. In order to understand microbial infiltration and control in wound dressings, a number of microbiological assays (MTT, MTS and live/dead) were completed using *E. Coli*, *P. Aeruginosa*, *S. Aureus* in an effort to understand how the morphological and 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 attached to microspheres were anchored at a micro-nanofluidic interface and the molecules electrophoretically extended. We demonstrated that both the DNA segmental correlation and equilibrium lengths increased as the slit height decreased. Furthermore, for extremely confined DNA where $h \leq 30$ nm, we observed reptation of the DNAs' 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.

5:20pm **BI+AS+NS-MoA11 Measuring DNA Looping Pathways using Nanofluidic Manipulation**, *M. Roushan, Z. Azad, H. Wang,* ***Robert Riehn***, NC State University

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 nm^2, 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 demonstrate 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.

2D Materials Focus Topic
Room: 310 - Session 2D+AS+BI+PS+SS-TuM

2D Materials: Surface Chemistry, Functionalization, Bio and Sensor Applications

Moderator: Richard Osgood, Columbia University

8:00am **2D+AS+BI+PS+SS-TuM1 Phase Engineering in 2D Transition Metal Dichalcogenides**, ***Manish Chhowalla***, Rutgers University **INVITED**

Two-dimensional transition metal dichalcogenides (2D TMDs) — whose generalized formula is MX_2, where M is a transition metal of groups 4–7 and X is a chalcogen — exhibit versatile chemistry and consist of a family of over 40 compounds that range from complex metals to semiconductors to insulator. Complex metal TMDs assume the 1T phase where the transition metal atom coordination is octahedral. The 2H phase is stable in semiconducting TMDs where the coordination of metal atoms is trigonal prismatic. Unlike mechanical exfoliation and chemical vapor deposition, chemical exfoliation of semiconducting layered TMDs yields monolayered nanosheets with heterogeneous atomic structure consisting of metallic (1T) and semiconducting (2H) phases. Metal (1T phase) to semiconductor (2H phase) transition can be achieved via mild annealing of exfoliated materials. Semiconductor to metal transitions can be achieved via chemistry. The 1T phase in *semiconducting* TMDs has scarcely been studied but it deserves urgent attention as it exhibits promise as a hydrogen evolution catalyst and as contact electrode in electronic devices. We will describe these phase transitions in semiconducting TMDs and provide examples of how we have learned to exploit them for covalent functionalization, enhanced catalytic and electronic performance.

8:40am **2D+AS+BI+PS+SS-TuM3 Transition Metal Nanoparticles on Single-Layer MoS_2: Structural, Electronic and Catalytic Properties**, ***Takat B. Rawal***, *D.T. Le, T.S. Rahman*, University of Central Florida

We will present results of density functional theory based calculations of the geometric and electronic structure of several types of sub-nanometer sized transition metal nanoparticles (TMNPs) on pristine and defect-laden single-layer MoS_2. We will show that among the investigated TMNPs (Cu, Ag, Au), Cu nanoparticles bind strongest to pristine MoS_2 while Au and Ag nanoparticles bind with similar, weaker strengths. The presence of the vacancy defect on MoS_2 enhances significantly the binding strength of Cu nanoparticles, while it has very little effect on the binding strength of Au NPs. More interestingly, the amounts of charge transfer from TMNPs to MoS_2 vary following the order of the bind energies of TMNPs on MoS_2. Additionally, the shape of the nanoparticles also has an impact on the binding characteristics. Of particular interest is the role of the substrate on the catalytic properties of the TMNP and conversely that of the TMNP on the defect-laden MoS_2 single layer. In this regard we will examine in detail the reactivity of the atoms at the TMNP/MoS_2 interface in reactions such as CO oxidation and methanol decomposition and compare them to that of similar nanoparticles when supported on titania.

Work supported in part by DOE Grant No. DE-FG02-07ER15842

9:00am **2D+AS+BI+PS+SS-TuM4 How Fluorination Enhances Friction Forces for Graphene**, ***Xin Liu***, *Q. Li,* University of Pennsylvania, *S.P. Kim,* Brown University, *V.B. Shenoy,* University of Pennsylvania, *P.E. Sheehan, J. Robinson,* Naval Research Laboratory, *R.W. Carpick*, University of Pennsylvania

The chemical functionalization of graphene can alter its electronic, chemical, mechanical, and tribological properties. Here we employ atomic force microscopy (AFM), Raman microscopy, and molecular dynamics (MD) simulations to show that friction can be fine-tuned by chemically modifying graphene. Although bulk fluorinated graphite has a very low surface energy, our experiments and simulations both show that friction between nanoscale tips and FG is up to 9 times higher than that for pristine graphene. The ability to resolve an ordered lattice in atomic stick-slip friction measurements also diminishes with greater fluorination, indicating that the fluorinated graphene is disordered. Our observation suggests that AFM friction measurements provide a sensitive local probe of the degree of fluorination of graphene. Motivated by MD simulations, we propose that the dramatic enhancement of friction results from increased corrugation of the interfacial potential due to the strong local charge concentrated at fluorine sites, consistent with the Prandtl-Tomlinson model.

9:20am **2D+AS+BI+PS+SS-TuM5 Chemical, Structural and Electrical Modification of Graphene**, ***Sandra Hernández***, *E.H. Lock, M. osofsky, S. Tsoi,* Naval Research Laboratory, *C. Junkermeier,* Penn State University, *R. Stine,* Nova Research, *J. Robinson,* Naval Research Laboratory, *A. Nath,* George Mason University, *V.D. Wheeler, R.L. Myers-Ward, J. Caldwell, C.R. Tamanaha, T. Reinecke, P.E. Sheehan, D.K. Gaskill, S.G. Walton*, Naval Research Laboratory

2D nanomaterials have been vigorously investigated due to their superlative mechanical, thermal, and electronic properties. Being composed entirely of surface atoms, they are incredibly amenable to surface modification thus providing the opportunity towards excellent control over their properties. Surface engineering of 2D materials composed of carbon materials, such as graphene, can be achieved by plasma modification. We will discuss our efforts in understanding the chemical, structural, and electrical properties of plasma functionalized graphene by introducing -oxygen, -fluorine, and -nitrogen chemical moities, and discuss their impact on chemical reactivity, electrical transport, and enhanced sensing behavior. Demonstrating how precise nano-engineering of surface chemistry impacts contact engineering, biosensing and device based applications.

This work is supported by the Naval Research Laboratory Base Program.

9:40am **2D+AS+BI+PS+SS-TuM6 The Mechanochemistry of Chemically Modified Graphene**, ***Jonathan Felts***, *S.C. Hernandez, A.J. Oyer, J. Robinson, S.G. Walton, P.E. Sheehan*, Naval Research Laboratory

Defining the optoelectronic properties of graphene through controlled chemical functionalization provides a route to fabricating a wide range of graphene based devices. In prior work, we showed that heat supplied by a scanning probe removed functional groups from chemically modified graphene (CMG) thereby restoring it to graphene [1]. Here we show that mechanical stress alone effectively removes functional groups. We measured the degree of surface functionalization by monitoring both normal load and friction between the sliding tip and a plasma processed CMG sheet. For oxygenated graphene, friction decayed exponentially with sliding distance, dropping to ~15% of the starting value. These measurements revealed an initial drop in friction that was independent of applied stress, suggesting the presence of an adsorbed water layer on the surface. More importantly, they reveal an Arrhenius-like relationship between contact stress and degree of surface reduction. The reduction in friction persisted, precluding the presence of the adsorbed contaminants as the source of the friction change. Conductive AFM and Raman measurements provide further evidence for chemical reduction. Conductive diamond AFM tips measure the current through the surface during the reduction process, revealing a 5x increase in conductivity corresponding to the friction force reduction. Additionally, Raman measurements on a 5 mm^2 reduced area showed a relative increase in both the G and 2D peaks, consistent with a reduction in functionalization. These experiments enabled detailed comparison of tribochemical reactions without the complications of 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 between the tip and a graphene surface functionalized with either oxygen or fluorine groups. For oxygenated graphene, the contact 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 supporting 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.

[1] Z. Wei, et al, *Science* **328**, 1373-1376 (2010)

11:00am **2D+AS+BI+PS+SS-TuM10 Fe-catalyzed Etching of Graphene, Few-Layer Graphene, and Graphite**, ***Guangjun Cheng***, *A.R. Hight Walker*, National Institute of Standards and Technology

Mechanically exfoliating graphite onto a substrate provides a family of layered materials with adjustable thickness, including monolayer graphene, few-layer graphene (FLG), and graphite. In this work, we investigated the Fe-catalyzed etching of graphene, FLG, and graphite in forming gas (10% H_2/90% N_2) or N_2 using low-voltage scanning electron microscopy and Raman spectroscopy. Fe thin films were deposited by sputtering onto mechanically exfoliated graphene, FLG, and graphite flakes on a Si/SiO_2 substrate. When the sample is rapidly annealed in either gas environment, particles are produced due to the dewetting of the Fe thin film and expected to catalyze the etching of graphene, FLG, and graphite. The combined microscopic and spectroscopic evidence reveals a thickness-dependent,

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

11:20am **2D+AS+BI+PS+SS-TuM11 Tunable Graphene/Si Schottky Diode Sensor: Before and After Functionalization for Wide Range of Molecular Sensing**, ***MdAhsan Uddin***, *A. Singh, T. Sudarshan, M.V.S. Chandrashekhar, G. Koley*, University of South Carolina

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 diode sensor exhibited 13 times higher sensitivity for NO_2 [Fig. 2(a)] and 3 times higher for NH_3 [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 NO_2 as the bias magnitude varied from -1 to -8V [Fig. 3(a)]. Optimized sensor design to detect particular analyte is also possible by careful selection of graphene/Si heterojunction SBH. For example, graphene/p-Si with larger SBH is better NO_2 sensor while smaller SBH device has better NH_3 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 NO_2 exposure while increased by 0.16eV for NH_3. Variation in sensitivity with NO_2 and NH_3 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 H_2. Extrapolated SBH from the I-V characteristics, before and after few nm metal decoration, and H_2 exposure showed initial SBH decrease after functionalization and subsequent increase in presence of H_2, respectively [Fig. 6(a) and (b)]. Compared to graphene chemiresistor, the chemi-diode sensor offers more than one order of magnitude higher H_2 sensitivity for both types of functionalization. Similarly, the reverse bias operation also enables low power consumption, tunable sensitivity and detection of H_2 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 varying H_2 concentration ranging from 2 to 1000 ppm [Fig. 7(c)].

12:00pm **2D+AS+BI+PS+SS-TuM13 Dielectrics 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 insulators 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 growth of high-k insulators. This study demonstrates 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. STS 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 at low bias. Multiple cycles of TMA and water were dosed onto O-TiPc/HOPG to investigate nucleation of Al_2O_3 on the O-TiPc layers. The first cycle of TMA was observed to chemisorb on a 1.4 x 1.4 nm grid on the TiOPc monolayer. After exposure O-TiPc monolayer to 5 cycles ALD pulse (tri-methyl-aluminum (TMA)+H_2O), insulating aluminum oxide was deposited uniformly on O-TiPc/HOPG. After formation of Al_2O_3 on O-TiPc/HOPG, the band gap of surface increases from 1.7 eV to 2.7 eV, while the conductance decreased. As shown in XPS spectra, the quality of Al_2O_3 can be improved by post annealing, consisting with transition of chemical states in O 1s peak and Al 2p. The chemical shifts of O and Al indicate that post annealing converts remained the Al-OH to Al_2O_3. Consequently, O-TiPc can not only act as a low-K dielectric but also induce high density ordered nucleation of ALD on central ion of O-TiPc for high-k dielectric growth.

Applied Surface Science
Room: 316 - Session AS+BI+VT-TuM

Ambient Ionization Mass Spectrometry

Moderator: Gerardo Brucker, Granville-Phillips Vacuum Products, Steven Pachuta, 3M Company

8:00am **AS+BI+VT-TuM1 Laser Ablation Electrospray Ionization Mass Spectrometry with Ion Mobility Separation for Cell and Tissue Analysis**, ***Akos Vertes***, *B. Shrestha, H. Li, S.A. Stopka, L. Zhang*, George Washington University **INVITED**

Laser ablation electrospray ionization (LAESI) is a novel ion source that enables the direct analysis of biological samples, including tissues and individual cells. In this ionization method, mid-IR laser ablation is followed by electrospray ionization of the ablated material in the expanding plume. Molecular coverage in complex biological samples is limited, in part, by the large number of components and the absence of a separation step prior to ionization. In addition, isobars, such as structural isomers and conformers, are not distinguished by mass analysis alone. To overcome these limitations, LAESI is combined with ion mobility separation (IMS) before mass spectrometry (MS). In this contribution, we describe the first results with such a LAESI-IMS-MS system for metabolite, lipid and protein analysis, including its application to plant and animal tissues, MS imaging and single cell analysis. The studied systems, among others, comprise mouse brain sections, *Arabidopsis thaliana* leaves and green algae (*Chlamydomonas reinhardtii*) cell pellets. The introduction of IMS resulted in enhanced molecular coverage, reduced interferences, distinction of structural isomers, observation of larger multiply charged ions typically suppressed by singly charged abundant metabolites and phospholipids, and in extended dynamic range.

8:40am **AS+BI+VT-TuM3 Miniature Mass Spectrometry Systems with Ambient Ionization and MS/MS Capabilities**, ***Zheng Ouyang***, *L. Li, Y. Ren, X. Wang, X. Ma, R. Zou, R.G. Cooks, Y. Xia*, Purdue University **INVITED**

As a technique for chemical analysis, mass spectrometry is versatile and provides very specific information. High sensitivity can be achieved when sample matrix effect is properly suppressed. Miniaturization of the mass spectrometry instrument system and simplification of the operation procedure enable the chemical analysis outside the analytical laboratories and/or by personnel without special trainings. The development of these systems goes beyond the miniaturization of the mass analyzers and mass spectrometers. At Purdue, we have taken an approach of combining the ambient ionization for direct sampling and the miniature ion trap mass spectrometer with MS/MS capability. The miniature systems use linear ion traps (LIT) for mass analysis and can perform multi-stage MS/MS, which help to improve the specificity of the analysis using the fragmentation pattern of the target analyst and to eliminate the chemical noise from the complex mixtures. A discontinuous atmospheric pressure interface (DAPI) has been developed to allow coupling of ionization sources at atmospheric pressure with the instruments using miniature pumping systems to support the vacuum. The DAPI opens for about 20 ms for ion introduction and requires a 200 ms delay for pressure drop prior to mass analysis. The complex gas dynamics has been characterized using direct simulation Monte Carlo method and an electro-hydrodynamic simulation method has been developed for predicting the ion trajectory for DAPI instrument design. While mass spectrometers as light as 4 kg have been previously developed with capability of analyzing non-volatile compounds, two complete MS analytical systems have recently developed as the backpack MS for in-field analysis and the Mini 12 desktop system for point-of-care analysis by nurses and physicians. These two systems use ambient ionization for direct sampling analysis. The low temperature plasma (LTP) probe was modified with an in-line configuration for point-and-shoot operation with the backpack MS. New ambient ionization methods have been explored for development consumable sample cartridges for the Mini 12 system, which include the paper spray, extraction spray and the most recent slug flow microextraction nanoESI. IS-coated capillary samplers have been developed for highly quantitative analysis using several microliters of biofluid samples and extremely operation procedures. On-cartridge chemical derivatization has been developed to significantly improve the sensitivity of the target analytes in complex biological samples and on-cartridge assays have also been studied for direct monitoring the

enzymatic functions. Direct analysis of the biological tissues have also been explored using Mini 12 and on-line Patenò-Büchi (P-B) reactions facilitated 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+BI+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 organics 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 types 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^{-4} 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+BI+VT-TuM6 A VAMAS Interlaboratory Study for Desorption Electrospray Ionisation Mass Spectrometry (DESI MS) - Survey of the Measurement Issues**, ***Paulina Rakowska***, *E. Gurdak, 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 do this. VAMAS provides an excellent mechanism for such evaluation. Under this framework, the National Physical Laboratory (UK) has conducted a DESI interlaboratory comparison. The objectives of this study were to determine the current achievable repeatability and constancy of instruments. The comparison was conducted with the involvement of 20 laboratories from 10 different countries. The instruments used included 7 commercially made DESI sources with the remainder home-built. A variety of mass spectrometers were used including 13 Ion Traps, 4 Orbitraps and 4 Time-of-Flight. Participants were provided with an analytical protocol and two reference samples: a thin layer of Rhodamine B and a double-sided adhesive tape. The studies comprised acquisition of positive ion mass spectra in pre-determined *m/z* ranges. No sample preparation was required. Results for Rhodamine B show that intensity repeatabilities below 20 % may be achieved. However, inadequacies of the spray and sample stage designs lead to repeatabilities that average 50 % with some worse than 80 %. Rhodamine B is an excellent reference sample to check the sample erosion, the sample stage movement and memory effects. The adhesive tape samples show that the absolute intensity repeatability is 31 % with several achieving below 20%. Importantly, the spectral response, given by the relative repeatability, not measurable with Rhodamine B, was reduced to 9 % with a significant number achieving the 5 % expected of more mature analytical methods. The constancy of these spectra from relative intensities gives day-to-day averages of 31 %, over three times worse than the short term repeatability. Significant differences in the spectra from different laboratories arise from different factors. This first interlaboratory study has provided an effective survey of the measurement issues and some important conclusions can be drawn about the possibilities for DESI MS concerning overall practice, reference samples and recommendations for the future. These will be discussed.

11:00am **AS+BI+VT-TuM10 Mass spectrometry surface analysis outside the vacuum**, ***Justin Wiseman***, *M.E. ElNaggar, J.K. Kennedy, B.L. Laughlin*, Prosolia Inc. **INVITED**

Advances in mass spectrometry in the last 20 years has produced instruments with higher resolving power, smaller footprints, even portable, and the capability of measuring surfaces for molecules in the ambient air; the former truly enabling the latter. Ambient mass spectrometry involves the characterization of samples in their native state in the open air and is exemplified by the development of Desorption Electrospray Ionization (DESI) and Direct Analysis in Real Time (DART). DESI uses high velocity charged droplets produced by a pneumatically-assisted electrospray to effect desorption and ionization of surface-bearing analytes. The applications of the technique are broad and span from the detection of leachables to thin-layer chromatography to imaging of drugs, metabolites and lipids in histological tissue sections, where the lateral spatial resolution has been reported to be as high as 50µm. The flowprobe, also an ambient technique, uses a liquid-microjunction formed at the surface to extract and deliver analytes to the mass spectrometer via an electrospray source. The applications of the flowprobe are also broad and have included microarray sampling, thin-layer chromatography plate analysis, and biological tissue analysis. This presentation will discuss the merits and applications of each of the DESI and flowprobe devices, with emphasis on their application to imaging biological tissue.

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

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 Ambient Ionization (AI), have simplified the applicability of API techniques by removing some or all of the need for sample preparation prior to analysis. AI techniques, such as Desorption Electrospray Ionization (DESI), Direct Analysis in Real Time (DART), and an ever increasing list of additional techniques and variations, allow for direct analysis of an enormous range of sample and matrix types; whole blood, illicit drugs in fingerprints, tissue cross-sections, pharmaceuticals, and forensic samples 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

8:20am **BI+AS+MN+NS-TuM2 An Inductive-Capacitive Sensor for Real-time Biofilm Growth Monitoring**, ***Ekaterina Tolstaya***, *Y.W. Kim, S. Chu, K.D. Gerasopoulos, W.E. Bentley, R. Ghodssi*, University of Maryland, College Park

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 biofilms on implanted or external biomedical devices, such as catheters, are difficult to treat. Traditional antibiotic therapies for biofilm infections often 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 1). The resonant frequency of the sensor was approximately 16 MHz in air at room temperature. A device sensitivity of 1140 Hz/dielectric was demonstrated using a known dielectric material (deionized water) (Figure 2). *Escherichia coli* W3110 biofilms were grown for 48 hours over the LC sensor and the resonant frequency of the sensor was measured every 80 seconds using a spectrum analyzer (Figure 3). As the biofilm grew over the device, an increase in the resonant frequency of the LC sensor was observed. This is due to the lower dielectric permittivity of the biofilm compared to that of the growth media (Luria Broth, ε ~80), which results in decrease in the capacitance of the sensor. In control experiments with water and air as the media, a slight decrease in the resonant frequency was observed. The resonant frequency shift over time is in good agreement with the natural trend of biofilm growth (Figure 4) [2, 3]. The results validate the use of LC sensing for continuous monitoring of biofilm growth. This sensitive and reliable detection scheme, as well as the capability for flexible substrate integration and wireless interfacing, can serve as a foundation for the development of microsystems for real-time biofilm monitoring for both clinical and environmental applications.

8:40am **BI+AS+MN+NS-TuM3 The Interplay of Electrode Materials and Biomaterials in a Catechol-Modified Chitosan-Based Sensor for Clozapine Detection**, ***Robert Dietrich***, *T.E. Winkler, H. Ben-Yoav, S.E. Chocron, E. Kim,* University of Maryland, College Park*, D.L. Kelly,* University of Maryland School of Medicine*, G.F. Payne, R. Ghodssi*, University of Maryland, College Park

We present a study of atomic layer-deposited TiN and electroplated Pt black (PtB) as candidate electrode materials to replace Au in a catechol-modified chitosan redox cycling system (Fig. 1) for the electrochemical detection of the antipsychotic clozapine (CLZ). In complex biological fluids like blood, interference from other electrochemically active species is a major challenge. The choice of electrode material is critical in addressing this challenge, as surface morphology and composition may produce a stronger and more reproducible CLZ signal, while shifting that signal away from potential interferents and improving the signal-to-noise ratio. Our electrochemical characterization results indicate that TiN is superior to Au as a sensor material, with a 2.6 times higher CLZ signal and a 3.2-fold lower variability.

Identifying electrode materials with high CLZ signal-to-noise ratio will greatly aid in translating our detection approach into a point-of-care monitoring system. Such a device will reduce the burden currently associated with CLZ due to safety and efficacy monitoring requirements [1], thereby improving the quality of life for people affected by schizophrenia. Our previous work [2] has relied on gold electrodes as a substrate for our catechol-modified chitosan films. These 5×5 mm² micro-fabricated planar gold electrodes serve as controls, which we further modified here with: TiN for its inert properties; and PtB for its high surface area and potential electrocatalytic activity (Fig. 2).

The fabricated electrodes were characterized using cyclic voltammetry. Bare Au yields an oxidative CLZ peak signal of 1.06±0.20 μA, compared to 5.20±2.26 μA when coated with chitosan-catechol (Fig. 3). TiN electrodes produce a signal of 2.00±0.26 μA bare, and 13.7±0.7 μA when modified. The combination of higher signal and lower variability with the TiN is likely due to its inert chemical properties which also propagate more repeatable biomaterial modification. We observed a secondary peak with gold as well as bare TiN electrodes, likely due to interference related to chloride or oxygen. Modified TiN revealed only a single, CLZ-related peak. Results show that, as expected, signals from the bare PtB electrodes were 3370 times higher than from Au. However, they exhibited large variation between experiments, indicating the need for electroplating optimization. Testing the PtB electrodes with the chitosan-catechol film should increase both CLZ signal and resolution. Ongoing work is also focused on glassy carbon electrodes, which are expected to yield high repeatability by eliminating potential interfering oxygen signals in the redox cycling system.

9:00am **BI+AS+MN+NS-TuM4 Characterization of an Amperometric Glucose Sensor on a Flexible Polyimide Substrate for Continuous Glucose Monitoring and Insulin Delivery through Single Device**, *X. Du, J.R. Motley, A.K. Herman,* ***Liney Arnadottir***, *G.S. Herman, X. Tan, J.F. Conley, Jr.,* Oregon State University*, W.K. Ward, R.S. Cargill, J.R. Castle, P.G. Jacobs*, Pacific Diabetes Technologies

Type 1 diabetes affects over one million people and every year more than 30,000 children and adults are diagnosed with type 1 diabetes in the United States alone. Patients with type 1 diabetes cannot produce their own insulin and depend upon glucose sensors to monitor their blood glucose and adjust insulin levels either by injection or an insulin pump. The continuous monitoring of glucose blood levels and automatic insulin release by an artificial pancreas is a promising alternative to current treatment options, and can significantly improve the comfort and quality of life for the patient. Here we introduce a flexible catheter with an integrated glucose sensor capable of both continuously measuring glucose levels and deliver insulin through a single catheter. The amperometric glucose sensor includes multiple Pt indicating electrodes, Ag/AgCl reference electrode, electrohydrodynamic jet (e-jet) printed glucose oxidase enzyme layers, and permselective membrane for optimal glucose response from the interstitial tissue. The compact design is integrated on a flexible polyimide substrate and requires high durability for all the components due to the small radius of curvature of the catheter. The e-jet printing provides digital patterning flexibility and highly precise deposition of the enzyme layer, which allows improved uniformity and accuracy of the glucose sensor. Here we will discuss characterization and optimization of the indicating and reference electrodes using electrochemical methods, scanning electron microscopy, X-ray photoelectron spectroscopy (XPS), and time of flight secondary ion mass spectrometry. XPS was used to confirm full glucose oxidase coverage of the indicating electrode. Electrochemical testing indicates that e-jet printed glucose oxidase inks are still active towards glucose oxidation after printing and subsequent deposition of the permselective membrane. The operation and characterization of a fully functional glucose sensor integrated onto a catheter will also be discussed.

9:20am **BI+AS+MN+NS-TuM5 Chemically Modifying Graphene for Biosensing and Interfacing with Biology**, ***Paul Sheehan***, Naval Research Laboratory*, S.C. Hernandez,* National Research Council*, N. Long,* Nova Research*, S.P. Mulvaney, J. Robinson,* Naval Research Laboratory*, R. Stine,* Nova Research*, C.R. Tamanaha, S.G. Walton*, Naval Research Laboratory **INVITED**

Graphene has many properties that are highly suited for biological studies. For instance, its atomic thinness, high electrical conductivity, and simple production methods are ideal for biosensing. As another example, graphene can be attached to arbitrary substrates to lend them the chemical flexibility of carbon while adding only an ultrathin coating. For both biosensing and biofunctionalization, it is critical to produce high quality films that are precisely modified with the desired chemistry. For biosensing, the sensor must be functionalized for specific receptor-ligand recognition such as DNA-DNA or antibody-antigen binding. We will discuss our strategies for functionalization and the successful detection of specific DNA hybridization biologically-active field-effect transistors (BioFETs) based on chemically modified graphene. We will then discuss our use of graphene to interface biology with materials ranging from polymers to dielectrics to semiconductors. Graphene's incredible thinness enables its inclusion in more traditional sensing platforms as a non-intrusive functionalization layer, discreetly lending its chemical flexibility to other, more inert materials without otherwise impacting the sensing device.

11:00am **BI+AS+MN+NS-TuM10 Bioresorbable Sensors and Electronics**, ***John Rogers***, University of Illinois at Urbana Champaign **INVITED**

A remarkable feature of the modern integrated circuit is its ability to operate in a stable fashion, with almost perfect reliability. Recently developed classes of electronic materials create an opportunity to engineer the opposite outcome, in the form of devices that dissolve completely in water, with harmless end products. The enabled applications range from 'green' consumer electronics to bio-resorbable medical implants – none of which would be possible with technologies that exist today. This talk summarizes recent work on this physically 'transient' type of electronics and sensors, from basic advances in materials chemistry, to fundamental studies of dissolution reactions, to engineering development of complete sets of device components, sensors and integrated systems.

11:40am **BI+AS+MN+NS-TuM12 Surface Chemistry Enhanced Microbial Bioelectrocatalysis**, ***Kateryna Artyushkova***, *C. Santoro, S. Babanova, J. Cornejo, L. Ista, A. Schuler, P. Atanassov*, University of New Mexico

Bioelectrochemical oxidation carried out by bacteria attached on a solid electrode is capturing the attention of scientists all over the world. Different species of bacteria have been shown as electroactive and being able to oxidize organic compounds releasing electrons that can be transferred to a conductive solid support. If the oxidation reaction is coupled with the oxygen reduction reaction (ORR), the degradation of organics could lead to a production of useful electricity and water. Those related aspects are currently utilized in the development of alternative and cost effective bioelectrochemical systems (e.g. microbial fuel cell (MFC)) for simultaneous organics removal and electricity production. Understanding

the bioelectrocatalytic nature of organics dissimilation by bacteria and the subsequent internal and external electron transfer is of a high importance for the further development of these systems and a key moment in their future application.

In this work, an artificial approach for enhanced microbial bioelectrocatalysis was explored along with study of the parameters promoting bacteria external electron transfer. 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 thiols to form self assembled monolayers (SAMs) with various functional groups ($-CH_3$, -OH, $-N(CH_3)_3$ 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 .

Biomaterial Interfaces
Room: 317 - Session BI+AS-TuA

Characterization of Biointerfaces

Moderator: Joe Baio, Oregon State University

2:20pm **BI+AS-TuA1 Comparative Study of the Bonding and X-ray Induced Reactions of Thiolated and Unthiolated DNA Adsorbed on Gold**, ***Richard Rosenberg***, Argonne National Laboratory, *J.M. Symonds,* Georgia Institute of Technology, *K. Vijayalakshmi,* Argonne National Laboratory, *D. Mishra,* Weizmann Institute of Science, Israel, *T.M. Orlando,* Georgia Institute of Technology, *R. Naaman*, Weizmann Institute of Science, Israel

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 by a process known as dissociative electron attachment (DEA). There is vast literature on the role of TNI states and DEA in DNA related radiation chemistry.[1,2] Due to its high flux density, synchrotron radiation (SR) has often been used to induce and study radiation chemistry in numerous systems,[3] including DNA and related molecules. SR has also been used to probe the electronic structure and bonding of such molecules, primarily by probing the occupied states with X-ray photoelectron spectroscopy (XPS) and the unoccupied states with X-ray absorption (XAS) measurements. Bond overlap and localization can be revealed by XPS while XAS can determine the density of unoccupied states and the orientation of the orbitals. In this presentation we examine X-ray induced reactions of DNA adsorbed on a gold substrate when the DNA is either thiolated (tDNA) or when it is unthiolated (uDNA). By performing polarization-dependent XAS at the N K edge we determined that tDNA protrudes from the surface at ~45 degrees, in agreement with previous studies. We also found that the unthiolated molecules have a similar orientation. However, due to differences in charge transfer between the gold and the DNA in the two systems there is a higher density of unoccupied states in the N-C=N derived π^* orbital for tDNA. We also found that the adsorbed tDNA has a significant higher cross section for radiation damage. The reason for this enhancement could arise from the greater probability of forming a TNI state for the tDNA due to the higher density of unoccupied π^* states.

1. E. Alizadeh and L. Sanche, Chem. Rev.**112**, 5578 (2012).

2. R. Naaman and L. Sanche, Chem. Rev.**107**, 1553 (2007).

3. R. A. Rosenberg and S. P. Frigo, in Chemical Applications of Synchrotron Radiation, Part II: X-ray Applications, edited by T.K. Sham (World Scientific Publishing Co., Singapore, 2002), Vol. 12A, p. 462.

2:40pm **BI+AS-TuA2 XPS Binding Energy Shifts for DNA Brushes on Gold**, *C.C.A. Ng,* ***Dmitri Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

DNA biointerfaces are important in a wide range of existing and emerging applications, such as biosensors, functionalization of nanoparticles for biomedical applications, and self-assembly of complex and functional nanostructures. The complexity of many of the DNA biointerfaces created for such applications often limits the ability to unambiguously interpret the results obtained from spectroscopy measurements for such systems. A powerful and successful approach to improving the analytical capabilities has been based on creating robust and well-defined reference systems, which then provide the insight for data interpretation in more complex analyses. Brushes of oligo(dT) single-stranded DNA can be attached to gold either via terminal thiol linkers, or via terminal blocks of (dA) nucleotides. While the former method results in a brush of roughly upright oligo(dT) strands relatively weakly interacting with one another, the complementarity of (dA) and (dT) blocks within the same strand creates a possibility of intra-strand hairpin-like hybrids in the (dA)-anchored case. Varying the parameters of these DNA brushes and deposition solutions creates a series with expected variation of thickness, surface density, and intra-strand interactions. Gold substrate provides a convenient binding energy (BE) reference for accurate XPS measurements of the characteristic DNA peaks. 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 **INVITED**

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 imaging1 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.

References

1 Nasse, M. J., Walsh, M. J., Mattson, E. C., Reininger, R., Kajdacsy-Balla, A., Macias, V., Bhargava, R., and Hirschmugl, C. J. (2011) Nat.Methods 8, 413-416

2 Martin, M. C., Dabat-Blondeau, C., Unger, M., Sedlmair, J., Parkinson, D. Y., Bechtel, H. A., Illman, B., Castro, J. M., Keiluweit, M., Buschke, D., Ogle, B., Nasse, M. J., and Hirschmugl, C. J. (2013) Nat.Methods 10, 861-864

Acknowledgements

This work was supported by the US NSF under awards CHE-0832298, CHE-1112433, and DMR-0619759, the Research Growth Initiative of the University of Wisconsin–Milwaukee, and is based on research conducted at the Synchrotron Radiation Center, University of Wisconsin–Madison which is supported by the University of Wisconsin– Milwaukee and University of Wisconsin–Madison.

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

The development of argon 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 Scurr***, 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 highlighted 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 a combination of ToF-SIMS and AFM analysis revealed the distribution of the active agents upon the surface which would be relevant to the the anti-microbial performance.

[1] Meeus, Scurr, Amssoms, Davies, Roberts, and Van den Mooter (2014) Molecular Pharmaceutics, 10 (8)

[2] Judd, Scurr, Heylings, Wan, and Moss (2013) Pharmaceutical Research, 30 (7)

[3] Liakos, Rizzello, Scurr, Pompa, Bayer and Athanassiou (2014) International Journal of Pharmacy, 463 (2)

5:00pm **BI+AS-TuA9 Analysis of Peptide Microarrays on Si Using ToF-SIMS**, ***James A. (Tony) Ohlhausen***, *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.

**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.

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 makeup 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 ERRB2. Images and spectra have been acquired on an IONTOF TOF.SIMS V using Bi_3^+. The ToF-SIMS information, combined with gene expression array analysis is used to investigate the chemical differences between chemotherapeutic 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 using ToF-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.

5:40pm **BI+AS-TuA11 Correlative Imaging of Mammalian Cells in Their Native Environments using a Microfluidic Reactor by ToF-SIMS and SIM**, ***Xin Hua****, C. Szymanski, Z.Y. Wang, B.W. Liu, Z. Zhu, J.E. Evans, G. Orr,* Pacific Northwest National Laboratory*, S.Q. Liu,* Southeast University, China*, X.Y. Yu*, Pacific Northwest National Laboratory

Mammalian cell analysis is of significant importance in providing detailed insights into biological system activities. Due to the complexity and heterogeneity of mammalian cell behavior and the technical challenge of spatially mapping chemical components in a hydrated environment, correlated chemical imaging from multiplexed measurement platforms is needed. Fluorescence structured illumination microscope (SIM), with super high resolution and visualization of proteins and sub-cellular structures in 3-D, provides more detailed information in cell imaging. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a unique surface-sensitive analytical tool that provides molecular information and chemical mapping with a sub-micron lateral resolution. However, the understanding of how the spatial heterogeneity and structural difference affect the mammalian cell activities in an unperturbed, hydrated state by ToF-SIMS is severely limited due to the challenge to detect liquids with high volatility under high vacuum environment using surface sensitive technique like ToF-SIMS.

We recently developed a novel microfluidic reactor for C10 mouse lung epithelial cell growth for SIM imaging and direct probing of hydrated cell in vacuum using ToF-SIMS. C10 cells were inoculated into the microchannel, incubated at 37 ^{o}C for 24 hr., fed with 5 nM quantum dots, and then fixed with 4% paraformaldehyde before SIM imaging. In subsequent ToF-SIMS analysis, an aperture of 2 µm in diameter was drilled through SiN membrane to form the detection window to image biological surfaces directly; and surface tension is used for holding the liquid within the aperture.

SIM images show that C10 cells are successfully cultured on the SiN membrane, and quantum dots are uptaken by cells and dispersed in the cytoplasm. The ToF-SIMS *m/z* spectra showing characteristic fragments of dried cell sample, hydrated cells, and uninoculated medium in the microreactor will be presented. Moreover, 2D images of representative cell fragments and quantum dots ion mapping will be discussed. In addition, depth profiling will be used to provide time- and space-resolved imaging of the cells inside the microchannel. Furthermore, principal component analysis is conducted to evaluate the intrinsic similarities and discriminations among samples. Our results demonstrate feasibility for *in situ* imaging of cells in the hydrated state using ToF-SIMS for the first time. Correlative imaging using SIM and ToF-SIMS provides information across different space scales for investigating cell dynamics. This novel approach has great potential for studying intracellular processes in the future.

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/C3NP70094A]. 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 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.

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

Chemical Imaging in 2D and 3D

Moderator: Jeffrey Fenton, Medtronic, Inc., Kathryn Lloyd, DuPont Corporate Center for Analytical Sciences

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 Vibrational Spectroscopy and Modelling Approaches**, *S. Roy, P.A. Covert, K.-K. Hung, U. Stege,* ***Dennis Hore***, 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 as 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. Kowalsky,* 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 thicknesses in the absence of light was first reported by Ito et al. on (8 hydroxyquinoline)aluminum(Alq_3), a prototypical fluorescent material used in OLEDs. It has been shown that the surface potential of Alq_3 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, Alq_3, on indium tin oxide (ITO) is investigated as a function of thickness using high resolution energy electron loss spectroscopy (HREELS), Raman spectroscopy, high resolution x-ray photoelectron spectroscopy (HR-XPS), attenuated total reflectance infrared spectroscopy (ATR-IR), and density functional theory (DFT) calculations. In order to provide a holistic understanding of the GSP, the results are compared to the vibrational spectra of 1,3,5-tris(N-phenylbenzimiazole-2-yl)benzene (TPBi) on ITO, an electron transporter host material with a measured GSP of 0.07 V/nm, and bis(triphenylsilyl)-dibenzofuran (BTDF) on ITO, a typical electron-conducting host used in combination with hole-conducting deep-blue emitter with a measured GSP of 0.08V/nm. The observed spectra show significant changes with the presence of the GSP in the organic material on ITO, which can be explained in terms of different symmetries of the isomers as well as between complexes and isolated anions. Additionally, it has been found that the surface phase differs from the bulk phase, where a structured layer is evident at the interface of the organic semiconductor, and this layer shifts with increasing thickness and in the presence of the GSP. The present work has provided direct evidence that

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. Pfaendtner,* 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 **INVITED**

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 Lütgebaucks***, *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. Dioleoylphosphatidylcholine (DOPC) and Dioleoylphosphatidylserine (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 solution, label-free, and substrate independent. Characterizing DOPC:DOPS composed 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 Vitro* and in Real Time Using Sum-Frequency-Generation Spectroscopy**, *P. Johansson, R. Francisco, J. Bryers,* ***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 vitro* character, typically involving purification steps. Here we show how to use sum-frequency-generation (SFG) spectroscopy to study early stages of amyloid fibrillar formation 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. fluorescence* 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.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Biomaterial Interfaces
Room: 317 - Session BI+MG-WeA

Design and Discovery: Biointerfaces
Moderator: Morgan Alexander, The University of Nottingham, UK

2:20pm **BI+MG-WeA1 Discovery of Materials for Stem Cell Control using Polymer Microarrays**, ***Morgan Alexander***, The University of Nottingham, UK

Polymer micro arrays have proven to be useful tools for the discovery of new synthetic materials which control cells.[1] This high throughput (HT) materials discovery approach is attractive because the paucity of understanding of the cell-material interface hinders the *ab initio* rational design of new materials.[2] The large number of polymer chemistries that can be investigated on a single polymer micro array act as a wide "net" in the search for materials that can achieve a certain cell response. Micro array *hits* are the starting point from which new materials may be developed.

Combinatorial acrylate libraries formed on standard glass slides were presented as a HT platform by Anderson and Langer of MIT.[3] To complement materials screening, we developed the approach of *HT surface characterisation* employing a range of analytical techniques in collaboration with the MIT group.[4] This surface characterisation step is necessary to directly relate the effect of the material on attached cells to the actual surface on which they sit, and to enable effective scale up from micro array to culture ware dimensions. Application of chemometrics, to handle the large amounts of complex data, reveals the importance of certain surface moieties, guiding the process of materials discovery and increasing our understanding of the cell-material interface.

We have applied this approach to the identification of materials which resist bacterial attachment and biofilm formation with application in the reduction of medical device centred infection.[5,6] In the mammalian cell field, we have identified materials which show promise as synthetic substrates for pluripotent stem cell culture.[7,8] These materials require pre-treatment with expensive proteins such as vitronectin, a constraint which limits their commercialisation.[9]

In this talk, screening of arrays with greater chemical diversity than ever before, incorporating up to 140 monomers[10], is reported which leads to the identification of materials which support pluripotent stem cell expansion without pre-treatment of the substrate with protein. Materials which support differentiation to mature cardiomyocytes which have potential application in in vitro toxicology screening have also been discovered.

1 Hook, A. L. **Biomaterials** (2010).

2 Kohn, J., **Nature Materials** (2004).

3 Anderson et al. **Nature Biotechnology** (2004).

4 Urquhart, A.et al. **Advanced Materials** (2007).

5 Hook, A. L. et al. **Nature Biotechnology** (2012).

6 Hook, A. L. et al. **Advanced Materials** *(*2013)

7 Mei, Y et al. **Nature Materials** (2010).

8 Saha, K. et al **PNAS** (2011).

9 Celiz, A. D et al. **Nature Materials** (2014).

10 Celiz, A.et al. **Biomaterials Science** (2014).

3:00pm **BI+MG-WeA3 Interfacial Force Field Parameterization in CHARMM for the Accurate Molecular Dynamics Simulation of Peptide Adsorption on High-Density Polyethylene**, ***Tigran Abramyan***, *J.S. Snyder, J.Y. Yancey, S.S. Stuart, R.A. Latour*, Clemson University

A fundamental molecular-level understanding of protein-surface interactions (PSIs) is crucial for many applications in biotechnology and bioengineering. All-atom molecular dynamic (MD) simulation methods hold great promise as a valuable tool for understanding and predicting PSIs. However, current MD force fields have not been validated for this application. In this study, adsorption free energy (ΔG_{ads}) of small TGTG-X-GTGT host-guest peptides (T = threonine, G = glycine, and X = variable amino acid residue) on a high-density polyethylene (HDPE) surface (110 crystalline plane) using the CHARMM force-field were calculated and compared with experimental results in order to find inaccuracies. In order to accurately calculate ΔG_{ads} in our simulation studies, advanced sampling methods such as umbrella sampling and replica-exchange MD were used to provide adequate conformational sampling of the peptides over the HDPE surface. Results revealed substantial discrepancies between the simulation and the experimental ΔG_{ads} values (i.e., differences exceeding 1.0 kcal/mol). To correct the adsorption behavior, an *in-house-developed* interfacial force-field (IFF) was incorporated into the simulation program with IFF parameters adjusted until satisfactory agreement with the experimental data set was achieved. Subsequent studies are planned to apply the tuned IFF to simulate the adsorption behavior of lysozyme and ribonuclease A proteins to HDPE, for which synergistically matched experimental studies have also been conducted to validate the developed method for protein-adsorption simulations.

3:20pm **BI+MG-WeA4 Degradable Silica Nanoshells for Ultrasonic Imaging and Therapy**, ***Alexander Liberman***, *C. Barback, R. Viveros, S.L. Blair, D. Vera, L. Ellies, R. Mattrey, W. Trogler, A.C. Kummel*, University of California at San Diego

As a safe alternative to intrasurgical guidewires and implantable radioactive seeds, gas-filled hollow Fe-doped silica particles have been developed, which can be used for ultrasound-guided surgery for multiple foci. The function of the Fe doping is to render the silica shells biodegradable. The particles are synthesized through a sol-gel method on a polystyrene template, and calcined to create hollow, rigid nanoshells. The Fe-doped silica shell is derived from tetramethyl orthosilicate (TMOS) and iron ethoxide, which forms a rigid, nanoporous shell upon calcination. The nanoshells are filled with perfluoropentane (PFP) vapor or liquid. The flourous phase is contained within the porous shell due to its extremely low solubility in water. *In vitro* studies have shown that continuous particle imaging time is up to approximately three hours non-stop. *In vivo* particle injection longevity studies have been performed in tumor bearing mouse models show signal presence with color Doppler imaging up to ten days post injection. To study biodistribution, nanoshells were functionalized with DTPA and radiolabeled with Indium-111 and then imaged by gamma scintigraphy over 72 hours. Scintigraphic imaging and gamma counting confirm that particles undergoing IV delivery to tumor bearing mice will passively accumulate in the tumors which may allow for tumor detection and therapuetic applications. Additionally, long term biodistribution studies in mice have shown a steady decrease in silicon content over the course of 10 weeks by inductively coupled plasma optical emmision spectroscopy (ICP-OES).

These silica shells break under acoustic excitation to release uncovered gas pockets which increase acoustic energy absorption and reduce acoustic cavitation threshold locally. Therefore they may also be employed as a sensitizing agent in high intensity focused ultrasound (HIFU) therapy. Traditional ultrasound agents which can be used as a HIFU senstizing agent pose several potential drawbacks such as poor *in vivo* persistence (minutes) and high risk during continuous perfusion. Preliminary *in vivo* HIFU ablation studies show that very few particles are needed in order to develop a sensitizing effect to HIFU thereby substantially reduce the amount of HIFU exposure necessary to achieve an ablative effect. It was found that nanoshells systemically adminstered to breast tumor bearing mice could be cavitated by HIFU 24 hours after administration. This mechanical cavitation caused liquification within the focal volume of the HIFU which contained the nanoshells within seconds of the HIFU application. This may potentially allow for a larger area to be ablated in less time with less power.

4:20pm **BI+MG-WeA7 An Encapsulation Technique for Adenovirus to Enhance Viral Gene Therapy**, ***Natalie Mendez***, *V. Herrera, L. Zhang, F. Hedjran, W. Trogler, S.L. Blair, A.C. Kummel*, University of California at San Diego

Oncolytic viruses (OVs) constitute a promising class of cancer therapeutics which exploit validated genetic pathways known to be deregulated in many cancers. To overcome an immune response and to enhance its potential use to treat primary and metastatic tumors, a method for liposomal encapsulation of adenovirus has been developed. The encapsulation of adenovirus in anionic 140-180nm diameter PEG containing non-toxic liposomes has been prepared by self-assembly of lecithin around the viral capsid. The encapsulated viruses retain their ability to infect cancer cells. Furthermore, an immunoprecipitation (IP) technique has shown to be a fast and effective method to extract non-encapsulated viruses and homogenize the liposomes remaining in solution. 76% of adenovirus plaque forming units were encapsulated and retained infectivity after IP processing. Additionally, encapsulated viruses have shown enhanced transfection efficiency up to 4X higher compared to non-encapsulated Ads. Extracting non-encapsulated viruses from solution may prevent an adverse in vivo immune response and may enhance treatment for multiple administrations.

4:40pm **BI+MG-WeA8 Sequential and Competitive Adsorption of Peptides at Pendant PEO Layers**, *X.W. Wu, M.R. Ryder, J.M. McGuire,* ***Karl Schilke***, Oregon State University

A more quantitative understanding of peptide entrapment and elution from otherwise protein-repellent polyethylene oxide (PEO) brush layers will provide direction for development of new strategies for drug storage and delivery. Here we describe criteria for peptide integration and structural change within the PEO brush, and discuss the reversibility of peptide entrapment with changing solvent conditions. For this purpose, three cationic peptides were used: the arginine-rich amphiphilic peptide WLBU2, the chemically identical but scrambled peptide S-WLBU2, and the non-amphiphilic homopolymer poly-*L*-arginine (PLR). Circular dichroism (CD) was used to record the adsorption and conformational changes of WLBU2 and S-WLBU2, and polyarginine peptides at PEO-coated silica nanoparticles. UV spectroscopy and a quartz crystal microbalance with dissipation monitoring (QCM-D) were used to quantify changes in the extent of peptide elution. Peptide conformation was controlled between disordered and α-helical forms by varying the concentration of perchlorate ion. We show an initially more ordered (α-helical) structure promotes peptide adsorption into the PEO layer. Peptide interaction with the PEO chains resulted in entrapment and conformational change that was irreversible to elution with changing solution conditions in the case of the amphiphilic peptide. In contrast, the adsorption and conformational change of the non-amphiphilic peptide was reversible. We also evaluated the effects of peptide surface density on the conformational changes caused by peptide-peptide interactions, and using CD, QCM-D, and UV spectroscopy, showed that these phenomena substantially affect the rate and extent of peptide elution from PEO brush layers. Specifically, for amphiphilic peptides at sufficiently high surface density, peptide-peptide interactions result in conformational changes which compromise their resistance to elution. In contrast, elution of a non-amphiphilic peptide is substantially independent of its surface density, presumably due to the absence of peptide-peptide interactions.

The sequential and competitive adsorption behavior of WLBU2, S-WLBU2 and PLR at pendant PEO layers was studied by optical waveguide lightmode spectroscopy (OWLS), time-of-flight secondary ion mass spectrometry (TOF-SIMS), CD and UV spectroscopy. Results strongly indicate that amphiphilic peptides are able to displace non-amphiphilic peptides that are adsorbed in PEO layers, while non-amphiphilic peptides cannot displace amphiphilic ones. In summary, peptides of high amphiphilicity are expected to dominate the competitive adsorption with less amphiphilic peptides in PEO layers.

5:00pm **BI+MG-WeA9 Moulding Cells and Materials in High Throughput**, ***Clemens van Blitterswijk***, *R. Truckenmuller, L. Moroni, N. Rivron, P. Habibovic, J. De Boer*, Maastricht University, The Netherlands **INVITED**

The interaction of cells and materials at their interface is crucial for the performance of devices that are applied in regenerative medicine.In general the approach to optimize interaction is characterized by a mechanistic low throughput research cycle where researchers try to move forward by improving performance based on fundamental insights and related small volume in vitro/in vivo experiments. Although this approach has successes it has its disadvantages. First as the field of regenerative medicine is young we currently lack fundamental insights into many of aspects that are relevant to our field.Second, the research cycle is slow, so if our experiments do not give the anticipated results we may lose several years.Third,the conventional approach only allows us to test a maximum of ca.10 experimental conditions in one cycle forces us to leave out many other possibly equally interesting, opportunities.

In our lab we are convinced on how influential surface geometry of material can be on cell behavior and in vivo response by recently inducing prominent bone formation in muscle tissue in large animals by modulating the biomaterial surface in the submicrometer range.The effects of these instructive materials are equivalent to the use of growth factors while no biological agents or cultivated cells were applied.As we have no complete insight in the underlying mechanism,a conventional low throughput

mechanistic approach does not seem the method of choice for further optimizing this performance and applying it to other tissue types.

Therefore,we developed multiwell screening systems that allow us to test a selection of thousands of surfaces from a truly designed high throughput library of 150 million different surface features in a single run. We have shown that this method allows us to modify cell shape and function in a remarkable way,both as far as cell attachment,proliferation and differentiation are concerned.As the above topochip platform is focused on 2D single cell performance and actual tissues are 3D and multicellular we have developed alternative platforms that allow us the build 3D mesoscale complex tissues in the thousands,while we have also generated so called 2,5 D muliwell systems that present convex surface features. Applying such systems allowed us to demonstrate that the mechanism of function follows form not only holds for individual cells but equally for millimeter scale cell aggregates.We are currently applying these technology platforms to create deeper insights in formation of tissues for regenerative medicine by introducing very early(embryonic)tissues in these systems while actively collaborating with developmental cell biologists.

6:00pm **BI+MG-WeA12 The Influence of Structural Array of Polymorphic hIAPP fibrils to its Mechanical Properties**, ***HyunJoon Chang***, *M. Lee,* Korea University, Republic of Korea*, G. Yoon,* Boston University*, S. Na*, Korea University, Republic of Korea

Amyloid proteins are misfolded, denatured proteins that are responsible for causing several degenerative and neuro-degenerative diseases, such as type II diabetes, Alzheimer's disease, Huntington's disease, and so on. Determining the mechanical stability of these amyloids is crucial for understanding the disease mechanism, which will allow us to provide guidance in treatment. Furthermore, many research groups also recognized amyloid proteins as a functional biological materials that can be used in nano sensor, bacterial biofilms, coatings, etc. There have been many *in vitro* studies to determine the material characteristics via force spectroscopy methods, Atomic Force Microscopy and Optical Tweezers to exemplify. However, computational methods (e.g. Molecular Dynamics (MD) and Elastic Network Model) not only reveal the mechanical properties, but also provide a more in-depth information on the amyloids by visualizing the conformation. In this study, we have discovered the material properties of four different polymorphic structures of Human Islet Amyloid Polypeptide (hIAPP) by using MD simulations under tensile Steered Molecular Dynamics (SMD) conditions. Also, from our results, we have observed how these mechanical properties may differ in respect of their structural formation. This study will help us to take a step forward for treating degenerative disease and also establish a template for the functional biological materials.

Scanning Probe Microscopy Focus Topic
Room: 312 - Session SP+AS+BI+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+BI+NS+SS-WeA1 Majorana Mode in Vortex core of Bi_2Te_3/$NbSe_2$Topological Insulator-Superconductor Heterostructure**, ***Jinfeng Jia***, Shanghai Jiao Tong University, China **INVITED**

Majorana fermions have been intensively studied in recent years for their importance to both fundamental science and potential applications in topological quantum computing[1,2]. Majorana fermions are predicted to exist in a vortex core of superconducting topological insulators[3]. 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_2Te_3/$NbSe_2$[4] by using *in situ* ultra-low 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_2Te_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:

1. J. Alicea, Rep. Prog. Phys.75, 076501 (2012).

2. C. W. J. Beenakker, Annu. Rev. Con. Mat. Phys. 4, 113 (2013).

3. L. Fu, C. L. Kane, Phys. Rev. Lett. 100, 096407 (2008).

4. M. X. Wang et al., Science 336, 52 (2012)

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

3:00pm **SP+AS+BI+NS+SS-WeA3 Robust Protection from Backscattering in the Topological Insulator $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$**, ***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 helically-spin-polarized surface electrons in a single and unwarped upper Dirac cone of $Bi_{1.5}Sb_{0.5}Te_{1.7}Se_{1.3}$. In this material [1], E_F is located very close to the Dirac energy E_D. We compared the scattering wave vectors observed at 5 K 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 [2]. 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/or 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 10 psec just above E_F. 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_F.

References

1. A. A. Taskin *et.al*, Phys. Rev. Lett. **109**, 066803 (2012).

2. S. Kim, *et al*, Phys. Rev. Lett. **112**, 136802 (2014).

3:20pm **SP+AS+BI+NS+SS-WeA4 Measurements and Analysis of Sub Nanometer Stepped Surfaces Using a Traceable Atomic Force Microscope**, ***Ndubuisi Orji***, National Institute of Standards and Technology (NIST)*, S. Gonda,* AIST, Japan*, R.G. Dixson*, National Institute of Standards and Technology (NIST)

Although scanning probe microscopes are used in a wide variety of nanoscale measurements, the issue of instrument characterization, accuracy and calibration, continue to be a limiting factor in interpreting the resulting data. In order to accurately characterize dimensional linearity and accuracy at the sub-nanometer range, samples and robust analysis techniques suited to measurements at this range should be used.

Using Al_20_3 surfaces on the c(0001), a(110), and r(102) planes, and robust analyses techniques, we evaluate stepped surfaces for linearity characterization at the nanoscale. Measurements were performed using a traceable atomic force microscope (T-AFM) with displacement interferometry in all three axes. The T-AFM, which has a metrology scanning stage monitored in six axes, is housed in a mini environment with a long term temperature range of less than 2 mK, and serves as a stable platform to develop calibration standards.

The smallest of the features Al_20_3 c(0001) with a height of 0.22 nm shows a combined uncertainty of 0.01 nm, with a linearity of 0.009%. The intrinsic traceability of the T-AFM (through displacement interferometer to the *SI* meter) provides additional verification to the size naturally occurring steps of the Al_20_3 and other samples used. The results show that robust and stable

linearization and calibration procedures could be developed for sub nanometer SPM characterization with low uncertainty. This will enable and support accurate dimensional characterization of scientifically relevant surfaces.

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

1D and 2D toplogical insulators (TI's) are characterized by 0D and 1D edge states of exotic spin-charge characteristics. In this talk, we introduce the first direct real space observations of such 0D and 1D edge channels of 1D and 2D TI's by scanning tunneling microscopy/spectroscopy. The 1D TI utilized is the charge density wave phase of In atomic wires formed on the Si(111) surface, which we discovered in 1999. We clearly identified, topographically and spectroscopically, two different soliton excitations along the wires. The unique features of these solitons, theoretically unraveled as chiral solitons of the Z_4 topology, are discussed. On the other hand, a Bi(111) bilayer was theoretically predicted as a 2D TI in 2005. We have grown Bi(111) bilayer nanoislands with zigzag edges on the surface of Bi_2Te_2Se. Along those edges, we identified the edge localized electronic state in accordance with first principle calculations. The unexpected electronic structures of the epitaxial Bi(111) bilayer and the Bi/Bi_2Te_2Se interface are discussed. These two findings pave the avenue towards the microscopic study and the nanoscale utilization of topological solitons and quantum spin Hall states.

5:00pm **SP+AS+BI+NS+SS-WeA9 Controlling Charges of the Dipole Layer at Metal-Semiconductor Interfaces**, ***Tae-Hwan Kim***, Pohang University of Science and Technology, Republic of Korea, *H.W. Yeom*, Pohang University of Science and Technology and Institute for Basic Science, Republic of Korea

Metal-semiconductor interfaces have drawn a lot of interest in the field of semiconductor surface and interface science, and have been one of the most essential parts in semiconductor electronic and optoelectronic devices. For example, the Schottky-barrier height experimentally observed at the metal-semiconductor interface appears to be nearly independent of the work function of the metal. Since the time of Bardeen, interface gap states seem to have been a primary mechanism of the Schottky-barrier height causing Fermi level pinning at metal-semiconductor interfaces. Recently, polarized chemical bonds at metal-semiconductor interfaces have been recognised to lead to the apparent Fermi level pinning effect. When these interface bonds are formed underneath thin metal islands grown on a silicon substrate, a spontaneous charge transfer across the semiconductor-metal interfaces occurs as a result of the difference in the Fermi level positions between the metal and the semiconductor. These polarized chemical bonds can form a dipole layer. This dipole layer can play an important role in many areas of technology, for instance, in organic light emitting diodes. However, some of the fundamental aspects of the charge injection process into/from the interface dipole layer at the Schottky contact are yet not explored in any real detail.

In this work, we report the use of scanning tunneling microscopy (STM) to form a double-barrier tunneling junction (DBTJ) with thin metallic nanoislands grown on Si(111) and to control charges of the interface dipole layer formed between the metallic nanoislands and the Si(111) substrate. Reversible hysteric switchings in their $I-V$ and differential conductance spectra are observed due to the charging and discharging of the interface dipole layer in a similar fashion to molecular DBTJs. STM images clearly visualize the distinct charge states and scanning tunneling spectroscopy (STS) spectra reveal that quantum well states (QWSs) of the ultrathin islands act as the charging/discharging channels in analogy to the molecular orbitals in the case of the molecular DBTJs. This work demonstrates that the charges of the interface dipole layer at the nanoscale Schottky contact can be controlled by the electron transfer via the QWSs of the metallic islands.

5:20pm **SP+AS+BI+NS+SS-WeA10 Advances in Imaging and Quantification of Electrical Properties at the Nanoscale using Scanning Microwave Impedance Microscopy (sMIM)**, ***Stuart Friedman***, *Y. Yang, O. Amster,* PrimeNano, Inc, *S. Johnston*, Stanford University

Scanning Microwave Impedance Microscopy (sMIM) is a novel mode for AFM-enabling imaging of unique contrast mechanisms and measurement of local permittivity and conductivity at the 10's of nm length scale. Custom shielded AFM probes enable the system to use microwaves to probe the impedance of the tip sample interface and extract information on local electrical properties of the sample. After introducing the theory of operation, we will review the state of the art, including imaging studies of microelectronic devices as well as novel materials and nanostructures, such as graphene and patterned optical crystals and ferro-electrics. These studies reveal novel information about doping distributions, domains, domain walls and other features. In addition to imaging, the technique is suited to a variety of metrology applications where specific physical properties are determined quantitatively. We will present research results on quantitative measurements of dielectric constant (permittivity) and conductivity (e.g. dopant concentration) for a range of materials. For samples where properties such as dielectric constant are known the technique can be used to measure film thickness.

5:40pm **SP+AS+BI+NS+SS-WeA11 Scanning Photocurrent Microscopy on MoS_2, $MoS_{2(1-x)}Se_{2x}$, and $MoSe_2$ Monolayer Islands and Films Grown by CVD**, ***Velveth Klee***, *D. Barroso, E. Preciado,* University of California - Riverside, *K. Erickson,* Sandia National Laboratories, *M. Triplett,* University of California -Davis, *C. Lee, A. Nguyen, I. Lu, S. Bobek, J. Mann,* University of California - Riverside, *A. Talin, F. Leonard,* Sandia National Laboratories, *L. Bartels*, University of California - Riverside

We presents scanning photocurrent measurements on CVD-grown monolayer films of molybdenum disulfide, molybdenum diselenide and the alloys of these materials. Our experiments reveal a pronounced effect of the current on excitation in the gap region between contacts, as opposed to directly at the electrodes. Measurements at different irradiation intensity, irradiation position and bias shed light on the charge transfer processes in this material system. Thermal effects are ruled out by complementary measurements of thermal transport using infrared imaging.

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

Fundamental Aspects and Imaging with the Ion Microscope

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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 (bio-) colloids, vesicles, granular matter, bacteria or technical multi-contact interfaces. The analysis must build on the small-load approximation, which states that the shifts in resonance frequency and resonance bandwidth are proportional to the in-phase and the out-of-phase component of the area-averaged stress at resonator surface. For realistic modeling, a numerical code is needed which predicts this stress field from the geometry and all materials parameters involved. There is such a model in two dimensions, building the finite element method.

On a simpler level, the behavior of particles on a resonator surface can also be understood from the coupled resonance model. The particles in contact form small resonators of their own, where the "particle resonance frequency" is determined by the mass and the stiffness of the contact. If the particle resonance frequency in the range of frequencies amenable to the QCM one observes a coupled resonance, meaning that the shifts of resonance frequency and resonance bandwidth themselves form a resonance curve when plotted versus overtone order. Depending on whether the particle resonance frequency is higher or lower than the QCM frequency, the frequency shift can be positive or negative. From the particle resonance frequency, one can assess the stiffness of the contact between the particle and the surface.

The detailed investigation of the coupled resonance picture reveals a problem. though. FEM models of the corresponding geometries reveal two coupled resonance, occurring at different frequencies. They corresponding to a rotation of the particle about the point of contact (the "rocking mode") and a rotation about the center of mass (the rotational mode"). The problem complicates the interpretation of experimental data, but it points to an intriguing analogy between QCM experiments a vibrational spectroscopy. A QCM experiment amounts to a vibrational spectroscopy on surface-attached colloids.

The last part of the talk is concerned with a novel sensing dimension of the QCM, which is the dependence of frequency and bandwidth on amplitude. Such dependences are ubiquitous in contact mechanics experiments and can be understood in terms of partial slip. The contacts behave nonlinearly. Nonlinear behavior can also be observed in liquids, where it is caused by the nonlinear term in the Navier-Stokes equation. The nonlinear term drives a steady flow of liquid along the direction of oscillation towards the center of the plate.

9:20am **QC+AS+BI+MN-ThM5 Study of Water Adsorption and Capillary Bridge Formation for SiO_2 Nanoparticle Layers by Means of a Combined *In Situ* FT-IR Reflection Spectroscopy – QCM-D Set-up**, ***Boray Torun***, *C. Kunze,* University of Paderborn, Germany, *C. Zhang, T.D. Kühne,* Johannes Gutenberg University Mainz, Germany, *G. Grundmeier*, University of Paderborn, Germany

During the past decade nanoparticles attracted a great deal of attention and found many applications in various fields ranging from pigments and antibacterial agents to highly effective catalysts. In this context, the handling and processing of nanoparticle powders play an important role. In contrast to macroscopic particles, nanoparticle flow properties are manly governed by the particle-particle 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. Hence, a fundamental understanding of the processes and forces involved plays a key role for the prediction of nanoparticle powder behavior.

In the presented study [1], water adsorption and capillary bridge formation within a defined layer of SiO_2 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 absorption spectroscopy (FT-IRRAS). On the one hand, the QCM-D gave insights on both, mass change (Δf) and changes in the contact mechanics, indicated by dissipation changes ($\Delta\Gamma$), whereas on the other hand FT-IRRAS allowed for the characterization 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 SiO_2 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 the qualitative and quantitative analysis of water adsorption and capillary bridge formation in particle layers.

[1] Torun, B. et al., *Phys. Chem. Chem. Phys.*, **2014**, 16, 7377-7384

9:40am **QC+AS+BI+MN-ThM6 On the Role of Acoustic Streaming in Particle Detachment Events at a QCM Surface**, ***Rebekka König***, *A. Langhoff, D. Johannsmann*, Clausthal University of Technology, Germany

A steady flow of liquid was observed above the surface of a quartz crystal microbalance (QCM) under conditions, where the oscillation amplitude exceeded 10 nanometers . The streaming flow occurs parallel to the displacement vector and is directed towards the center of the plate. It is expected to have applications in acoustic sensing, in microfluidics, and in micromechanics in a wider sense. The flow is caused by the nonlinear term in the Navier- Stokes equation, which can produce a nonzero time-averaged force from a periodic velocity field. Central to the explanation are the flexural admixtures to the resonator's mode of vibration. Unlike pressure-driven flows, the acoustically driven steady flow attains its maximum velocity at a distance of a few hundred nanometers from the surface. It is therefore efficient in breaking bonds between adsorbed particles and the resonator surface. As a side aspect, the flow pattern amounts to a diagnostic tool, which gives access to the pattern of vibration. In particular, it leads to an estimate of the magnitude of the flexural admixtures to the thickness-shear vibration.

[1] R. König, A. Langhoff, D. Johannsmann, *Physical Review E***2014**.

11:00am **QC+AS+BI+MN-ThM10 QCM for Particle Sizing and Beyond**, ***Adam Olsson***, *I.R. Quevedo, D. He, M. Basnet, W. Lee, N. Tufenkji*, McGill University, Canada **INVITED**

The dissipative energy loss of a quartz crystal microbalance (QCM) sensor is typically ascribed to the viscoelastic nature of the adsorbed material. While such an interpretation is suitable for thin homogeneous films, it is not *a priori* valid for discrete objects. As demonstrated recently, dissipation due to nanoparticle deposition can be described by the relative movement of the particles attached to the oscillating sensor surface. This particular dissipation behavior of nanoparticles gives rise to new experimental

approaches to study colloidal transport, particle-surface interactions and particle properties.

In this presentation, we focus on QCM-D as a method to determine the size of deposited nanoparticles. The approach involves analysis of the change in dissipation per attached mass (i.e., the "$\Delta D/\Delta f$-ratio") to predict a hypothetical full particle surface coverage that can be used to calculate an effective layer thickness of the particulate 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 sizes obtained from dynamic light scattering (DLS) and transmission electron microscopy (TEM). We found that accurate particle sizing is possible, but requires firm coupling between the particle and the sensor surface. Hence, if the particle size is known, the approach can also be used to investigate 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 anisotropic bacteriophage to determine their orientation on the surface. Bacteriophages are viruses that bind to and infect bacteria with high specificity and, thus, can be exploited in antimicrobial and biosensor applications. One challenge in functionalizing surfaces with bacteriophages is to control their orientation such that their binding sites remain exposed to the ambient medium. By studying how dissipation changes with phage surface coverage, it is possible to identify at which surface coverage phage-phage interaction occurs. This event compromises the phages ability to bind to bacteria, as evidenced by subsequent bacterial "capture" experiments and imaging, and thus is crucial for the performance of QCM-D based biosensors that utilize bacteriophage as a biorecognition element.

11:40am **QC+AS+BI+MN-ThM12 Full Experimental Proof of the Relationship between the Intrinsic Viscosity of DNA and the Acoustic Ratio of SAW and TSM Sensors**, ***Achilleas Tsortos***, IMBB-FORTH, Greece, *G. Papadakis,* NCSR-Demokritos, Greece, *E. Gizeli*, IMBB-FORTH & Univ. of Crete, Greece

Acoustic wave sensors are extensively used in biotechnology and biophysics in order, for example, to detect molecules in a solution, study an antibody-antigen interaction or the hybridization of DNA. Today, data analysis includes (a) the use of the Sauerbrey equation, in order to calculate the mass of the molecules attached on the surface of the acoustic device by use of frequency data and (b) the use of complicated mathematical models of the assumed 'film' formed by the attached molecules. In the second case information such as the rigidity modulus and viscosity of the 'film' can be calculated and comments can be made on the softness (viscoelasticity) of the added layer.

Here, we present an entirely different approach. Based on a theory developed earlier[1,2] we correlate the acoustic ratio R, to the intrinsic viscosity $[\eta]$ of the attached molecule. The acoustic ratio is the ratio of the amount of energy loss per attached unit mass – this is given as ($\Delta D/\Delta F$) in the TSM acoustic mode notification, or as ($\Delta A/\Delta Ph$) in the SH-SAW mode and is readily obtained in each experiment. The *intrinsic* viscosity on the other hand, is a hydrodynamic quantity directly related to the size and shape of a biomolecule and can be determined independently through viscometry. In this study we present collected experimental data from a variety of case studies proving for the first time the semi-empirically assumed relationship $R \sim [\eta]$ in a general form. Data are presented for various shapes and sizes of DNA and other systems of biological interest. The case is made for two acoustic modes (thickness shear and surface horizontal) and for various frequencies in the range of 5-155 MHz.

Our analysis presents a paradigm shift and challenge; we claim that (label-free) structure probing is a much more improved method offering higher flexibility in design and interpretation of experimental assays. Detecting and monitoring in real time processes that involve structural changes but not necessarily mass changes and/or 'film' formation is a novel concept that can be readily applied in anything from DNA, RNA hybridization and detection of mutations to molecular machines (e.g. DNA Holliday junction) and protein/DNA/RNA interactions in the broad areas of biophysics, s tructural DNA nanotechnology and diagnostics.

Acknowledgement: the REGPOT-InnovCrete/EU-FP7 (Contract No. 316223) for financial support.

References:

1. A. Tsortos, et al., *Biophys. J.* 2008, 94:2706

2. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836

12:00pm **QC+AS+BI+MN-ThM13 Characterization of the Conformation of Linker-Suspended Proteins at Surfaces through Acoustic Ratio Measurements**, ***Electra Gizeli***, IMBB-FORTH & Univ. of Crete, Greece, *D. Milioni,* IMBB-FORTH, Greece, *G. Papadakis,* NCSR-Demokritos, Greece, *A. Tsortos*, IMBB-FORTH, Greece

Characterization of protein shape and orientation following surface binding is an area of great interest in biophysics with many applications in chemistry and nano/biotechnology. Techniques such as ellipsometry and AFM have been extensively used for providing such information. A lot of effort has also been put with acoustic sensors; results in this case though depend greatly on the data interpretation model employed. An important question is always the preservation of protein integrity/form.

In this work we employ acoustic devices based on a QCM geometry at 35 MHz. The acoustic ratio $\Delta D/\Delta F$, i.e., the dissipation over frequency change of the shear wave has been employed in our analysis. We have previously shown[1] that as a tool, this ratio provides valuable information regarding the conformation of surface attached DNA molecules; we have also employed this approach in the design of DNA assays for diagnostic purposes, including detection of sequence targets in real samples[2].

Here we expand this methodology in proteins; streptavidin is used as a case study for characterizing spherical protein immobilization on an acoustic device. Good control of the binding mode was achieved by changing the distance of the protein from the surface, ranging from zero (direct physisorption) to several nm, using anchor molecules. In this way we can manipulate the degree of surface interference to the protein structure. Our results clearly show that direct protein adsorption is a multistep process resulting in very low acoustic ratio, in agreement with the literature. However, we show for the first time that suspending the protein away from the surface from a single point through a variable-length linker, gives an entirely different picture; the process is a single-step event, as judged from D-F plots, and the resulting acoustic ratio is much higher (order of magnitude) than that obtained in physisorption. The effect of the linker length on the apparent acoustic ratio is analyzed. This approach gives more reliable and different information regarding the protein shape than do simple physisorption protocols and interpretation models involving notions such as 'film' formation etc.

References:

1. A. Tsortos, et al., *Biosens. Bioelectron.* 2008, 24:836; A. Tsortos et al., *Biophys. J.* 2008, 94:2706

G. Papadakis et al., *Anal. Chem.* 2012, 84:1854; G. Papadakis et al., *Scientific Rep.* 2013, 3:2033

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, Characteristaion and Challenges**, ***Sally McArthur***, Swinburne University of Technology, Australia **INVITED**

Plasma polymers, the dogma tells us are densly 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 respnses 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 **INVITED**

"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 fed into a 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 nanocontainers carrying an antimicrobial to treat bacterial infection.

9:20am **SM+AS+BI+PS-ThM5 Plasma Modification of Drug-Eluting Materials for Localized Action at Medical Device Interfaces**, *J. Joslin, A. Pegalajar-Jurado, M.J. Hawker, E.R. Fisher,* ***Melissa Reynolds***, Colorado State University **INVITED**

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 H_2O(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.

11:00am **SM+AS+BI+PS-ThM10 Plasma Treated Substrates Reduce Protein Adsorption**, ***Marvin Mecwan***, *J. Stein, W. Ciridon,* University of Washington, *X. Dong,* Eli Lilly and Company, *B. Ratner*, 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 addressing the manufacture, 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 hydrophilic monomer plasma treated substrates had lesser protein adsorbed on their surfaces (< 2ng/cm^2) as compared to hydrophobic plasma treated substrates (10-14 ng/cm^2). This is in comparison to untreated controls that had 200-300 ng/cm^2 protein adsorbed on the surface. Furthermore, following ISO 10993-5 guidelines, by performing cytotoxic 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.

11:20am **SM+AS+BI+PS-ThM11 Modification of Porous Materials by Low Temperature Plasma Treatment to Achieve Low-Fouling Membranes**, ***Adoracion Pegalajar-Jurado***, *B.D. Tompkins, E.R. Fisher*, Colorado State University

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 H_2O 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.

11:40am **SM+AS+BI+PS-ThM12 Immobilized Laminin Concentration Gradients on Electrospun Fiber Scaffolds for Controlled Neurite Outgrowth**, ***Nicole Zander***, US Army Research Laboratory, *T. Beebe Jr.*, University of Delaware

Neuronal process growth is guided by extrinsic environmental cues such as extracellular matrix proteins (ECM). Recent reports have described that the growth cone extension is superior across gradients of the ECM protein laminin compared to growth across uniformly distributed laminin. In this work, we have prepared gradients of laminin on aligned electrospun nanofibers for use as substrates for neuronal growth. The substrates therefore presented both topographical and chemical guidance cues. Step gradients were prepared by the controlled robotic immersion of plasma-treated polycaprolactone fibers reacted with N-hydroxysuccinimide into the protein solution. The gradients were analyzed using x-ray photoelectron spectroscopy and confocal laser scanning microscopy. Gradients with a dynamic range of protein concentrations were successfully generated and neurite outgrowth was evaluated using neuron-like PC12 cells. After 10 days of culture, PC12 neurite lengths varied from 32.7 ± 14.2 μm to 76.3 ± 9.1 μm across the protein concentration gradient. Neurite lengths at the highest concentration end of the gradient were significantly longer than neurite lengths observed for cells cultured on samples with uniform protein coverage. Gradients were prepared both in the fiber direction and transverse to the fiber direction. Neurites preferentially aligned with the fiber direction in both cases indicating that fiber alignment has a more dominant role in controlling neurite orientation, compared to the chemical gradient.

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 Olsson, 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 free fatty acids and the structure of ceramide have 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**, ***Xia Dong***, *C.A.J. Kemp, Z. Xiao*, Eli 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 at higher concentration on gold than on 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 coupons will be further studied to understand the influence of surface morphology.

3:20pm **QC+AS+BI+MN-ThA4 Combining Spectroscopic Ellipsometry and Quartz Crystal Microbalance to Study Biological Hydrogels – Towards Understanding Nucleo-Cytoplasmic Transport**, *N.B. Eisele, S. Ehret, R. Zahn,* CIC biomaGUNE, Spain, *S. Frey, D. Gorlich,* MPI 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 disordered proteins (so called FG nups) that fills the nuclear pores (i.e. the roughly 40 nm wide channels across the nuclear envelope) and controls the entry of macromolecules into the nucleus of eukaryotic cells. The permeability barrier exhibits a unique selectivity in transport: very small molecules can cross the barrier efficiently, while larger objects are delayed or blocked unless they are bound to specialized proteins, so called nuclear transport receptors (NTRs). How size and species selectivity are encoded in the hydrogel-like properties of the permeability barrier is currently not well understood.

We have developed monolayers of end-grafted FG nups as a nano-scale model system of the permeability barrier. The planar geometry of this well-defined biomimetic film affords detailed and quantitative characterization – not accessible for the native system - with a toolbox of surface-sensitive characterization techniques. In particular, we present the application of the *in situ* combination of quartz crystal microbalance (QCM-D) and spectroscopic ellipsometry (SE) to quantify film thickness, hydration and viscoelastic properties as a function of protein surface density.

We will present how this experimental data, combined with polymer theory, allows us to better understand the relationship between the supramolecular organization and dynamics of the permeability barrier, its physico-chemical properties and its biological function. We demonstrate that attractive interactions between FG nups play an important role in tuning the assembly and morphology of FG nup meshworks, and highlight that even rather weak interactions – typically a few *kT* per biopolymer chain – have functional importance. We show also how the interaction between NTRs and FG nup meshworks is tuned to afford strong enrichment and at the same time rapid entry and exit of NTRs in the permeability barrier, thereby facilitating NTR translocation.

Taken together, these studies contribute important information to understand the mechanism of size-and species-selective transport across the nuclear pore permeability barrier. The mechanistic insight gained should be useful towards the design of bioinspired species-selective filtering devices. Moreover, the presented procedures for the acquisition and analysis of combined QCM-D/SE data are broadly applicable for the characterization of ultrathin biomolecular and other polymer films.

4:00pm **QC+AS+BI+MN-ThA6 Probing Nanoparticle-Biofilm Interactions using Quartz Crystal Microgravimetry and Complementary Surface-sensitive Methods**, ***Kaoru Ikuma****, University of Massachusetts, *Z. Shi, A.V. Walker,* University of Texas at Dallas, *B.L.T. Lau*, University of Massachusetts

The environmental fate and transport of nanoparticles (NPs) have been a rising topic of concern due to the increased use of nanotechnology. Recent studies have shown that NPs are likely to interact readily with and accumulate in environmental biofilms. Biofilms are a ubiquitous form of microbial presence where cells attached on solid surfaces are surrounded by a sticky matrix of extracellular polymeric substances (EPS). The EPS matrix is considered to be highly heterogeneous and chemically complex. Polysaccharides and proteins are known to be major constituents of EPS and may greatly impact the likelihood of interactions occurring between NPs and biofilms.

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-Fe_2O_3) NPs onto protein-coated silica surfaces were quantitatively measured by quartz crystal microbalance with dissipation (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 Kelvin probe force microscopy and time-of-flight secondary ion mass spectrometry (TOF SIMS) were used to characterize the mechanisms of interaction between the NPs and the protein-coated surfaces.

QCM-D results indicated 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

---

*** QCM Focus Topic Young Investigator Award**

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 Entrapment of Membrane-Targeted Nanoparticles with Different Binding Avidity: A QCM-D and sIngle Particle Tracking Study**, ***Anders Lundgren****, *B. Agnarsson, S. Block, F. Höök*, Chalmers University of Technology, Sweden

Nanoparticles specifically targeted to receptors in the cell membrane are interesting 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/entrapment of biotin functionalized core-shell nanoparticles to supported lipid bilayers sparsely modified with streptavidin. Gold-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 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 the mobility of single particles displaying diffusion constants close to 0.4 or 0.8 $\mu m^2/s$ irrespective of particle size, which was similar to ensemble measurements using FRAP data on FITC-labelled streptavidin (0.5 $\mu m^2/s$). 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 decreasing dissipative response per particle for binding of particles with increasing ligand density. Together, QCM-D and particle tracking data indicates that two different mechanisms may lead to particle trapping and ultimately particle wrapping: For very high ligand densities membrane receptors in the membrane diffuse to and partly wraps around immobile particles, whereas for intermediate ligand densities the diffusion and dynamics of the particles themself facilitate the formation of additional surface bonds and eventual wrapping.

4:40pm **QC+AS+BI+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, is a burgeoning new field that may break the existing boundaries of biomolecule applications in exclusively biological context. Extensive studies have already been performed in bioelectronics 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 chemiresistors 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 of gold 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 $\Delta R/R$ 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+BI+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 are 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 ppAAc 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+BI+MN-ThA10 Applications of QCM in Industrial R&D**, ***Andrey Soukhojak***, 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+BI+PS-ThA

Plasma Processing of Biomemetic Materials

Moderator: Sally McArthur, Swinburne University of Technology, Adoracion Pegalajar-Jurado, Colorado State University

2:20pm **SM+AS+BI+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 potentialities 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

*** QCM Focus Topic Young Investigator Award**

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+BI+PS-ThA3 Advantages of Plasma Polymerized Surfaces for Cell Sheet Engineering over Other Deposition Techniques**, ***Heather Canavan***, *M.A. 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, ~32oC), 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 thermoresponse and surface chemistry using X-ray photoelectron spectroscopy and goniometry. We find that plasma polymerized NIPAM substrates (ppNIPAM) are more stable under a variety of storage conditions prior to their use. Furthermore, when used for cell culture, ppNIPAM 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+BI+PS-ThA6 Biofunctionalization of Surfaces by Energetic Ion Implantation: Fundamentals and Recent Progress on Applications**, ***Marcela Bilek***, *A. Kondyurin, E. Kosobrodova, G. Yeo,* University of Sydney, Australia, *S. Wise,* Heart Research Institute, Australia, *N.J. Nosworthy, C.G. dos Remedios, A.S. Weiss, D.R. McKenzie*, University of Sydney, Australia **INVITED**

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.

4:40pm **SM+AS+BI+PS-ThA8 Three-Dimensional Biopolymeric Scaffold Surface Modification Using Plasma Enhanced Chemical Vapor Deposition: The Effect of Functionality and Wettability on Cell and Bacterial Attachment**, ***Morgan Hawker***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Three-dimensional (3D) bioresorbable polymeric materials, such as porous scaffolds made of poly(ε-caprolactone) (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 biomaterial development. Here, we demonstrate the deposition of conformal 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 (C_3F_8) and hexafluoropropylene oxide (HFPO) precursors were chosen as model hydrophobic film PECVD systems, whereas a copolymerization system consisting of allylamine/allyl alcohol (allylNH/allylOH) precursors 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. C_3F_8 and HFPO PECVD on scaffolds resulted in 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 allylNH/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+BI+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 work. 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 process. A number of approaches have 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 wounding 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.

Probing Chemical Reactions at the Nanoscale

Moderator: Carl Ventrice, Jr., University at Albany-SUNY, Jun Nogami, University of Toronto, Canada

2:20pm **SP+AS+BI+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 environment of Torr or even tens of Torr pressure range. 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 visualized. Surface structures of catalysts only formed 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 from one specific binding site 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 reactant gases. In addition, the in-situ studies of Pt(110) and Rh(110) during CO 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. Karayaylalı,* ***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. Karayaylalı 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, our results reveal that only modest gains of ~15% in 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 AlGaAs/GaAs Heterostructures by Kelvin Force Microscopy**, *S. Pouch,* ***Nicolas Chevalier***, *D. Mariolle, F. Triozon, Y.M. Niquet, T. Melin, Ł. Borowik*, 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 AlGaAs/GaAs heterostructures. For this study, we used a certified reference sample (BAM-L200), which is a cross section of GaAs and $Al_{0.7}Ga_{0.3}As$ epitaxially grown layers with a decreasing thickness (600 to 2 nm) and a uniform silicon doping ($5x10^{17}$ cm^{-3}). 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 meV between $Al_{0.7}Ga_{0.3}As$ 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 AlGaAs/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 $Al_{0.7}Ga_{0.3}As$ and 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 microscope (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

[1] J. Guo, X. Z. Meng, J. Chen, J. B. Peng, J. M. Sheng, X. Z. Li, L. M. Xu, J. R. Shi, E. G. Wang*, and Y. Jiang*, "Real-space imaging of interfacial water with submolecular resolution", Nature Materials 13, 184 (2014).

[2] J. Chen, J. Guo, X. Z. Meng, J. B. Peng, J. M. Sheng, L. M. Xu, Y. Jiang*, X. Z. Li*, E. G. Wang, "An unconventional bilayer ice structure on a NaCl(001) film", Nature Communications 5, 4056 (2014).

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,* Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland, *Y. Zhao, J.E. Wyrick, J.A. Stroscio,* NIST, *H. Brune*, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland

Inelastic electron tunneling spectroscopy (IETS) with the scanning tunneling microscope (STM) has vastly fueled the study of magnetic, electronic and vibrational properties of individual atoms and molecules due to its unmatched spatial and excellent energy resolution. Recently [1,2], rotational excitations could be characterized with IETS for the first time and yielded valuable insights into surface dynamics, bond lengths, and, notably about the nuclear spin state of homonuclear molecules. In particular, the two alike nuclei induce symmetry constraints in consequence of the Pauli principle and a certain alignment of nuclear spins requires a specific set of rotational levels *J.* We demonstrate rotational excitation spectroscopy (RES) with the STM for hydrogen, its isotopes, and mixtures thereof, physisorbed on metal supported graphene and hexagonal boron nitride, as well as on exfoliated graphene devices. We observe excitation energies that are equivalent with rotational transitions (ΔJ = 2) of molecules in the gas phase for hydrogen, hydrogen-deuteride, and deuterium, respectively. Notably, these values represent the nuclear spin isomers *para*-H_2 and *ortho*-D_2. For HD, an additional $J = 0 \rightarrow 1$ transition is discerned, which is allowed for heteronuclear diatomics. We discuss the excitation mechanism in the light of resonant enhanced tunneling [3,4], and illustrate how the

dynamics of molecules could be controlled by applying an electric field using a back gating graphene device geometry [5].

[1] F. D. Natterer, F. Patthey, H. Brune, *Phys. Rev. Lett.* **111**, 175303 (2013)

[2] Li *et al., Phys. Rev. Lett.* **111**, 146102 (2013)

[3] F. D. Natterer, F. Patthey, H. Brune, *arXiv*:1403.1312 (2014)

[4] B. N. Persson, A. Baratoff, Phys. Rev. Lett. **59**, 339 (1987)

[5] J. Chae *et al.,Phys. Rev. Lett.* **109**, 116802 (2012)

Funding from the Swiss National Science Foundation under project number 148891 is greatly appreciated.

Biomaterial Interfaces
Room: Hall D - Session BI-ThP

Biomaterial Interfaces Poster Session

BI-ThP2 Electroassembled Cell Populations in Microfluidic Gradient Generators for Biomolecule Screening, ***Chris Wolfram***, University of Maryland, College Park, *X. Luo,* The Catholic University of America, *H.C. Wu, C.Y. Tsao, M. Guo, G.W. Rubloff, W.E. Bentley, H. Sintim*, University of Maryland, College Park

Laminar flow at the microscale has led to the development of novel new methods for the generation of stable, highly controllable gradients in microfluidic devices. These well-characterized devices have enabled the study of bacterial behavior in complex microenvironments, as well as quantifying the strength of their response to varying concentrations of small molecules. However, flow-based gradient generators subject bacterial cells to shear stress which can attenuate any observed response and make single cell tracking difficult. Static gradient generators eliminate this effect, but the established gradient decays as a function of time due to diffusion. Entrapping cell populations in hydrogels protect them from turbulent environmental conditions, allowing for the use of flow. Additionally, spatially constraining these cells in an array subjects individual cells to the same local concentration without continual gradient deterioration.

The use of electroaddressable hydrogels has been previously demonstrated as a platform for biofabricating "model biofilms." Entrapping populations of *E. coli* in these stimuli-responsive polysaccharide hydrogels enables bacterial signaling interrogation in microfluidic environments with high precision. This technique is integrated within a flow-based microfluidic gradient generator as a device for probing the comparative effects of signaling molecules and nutrients on *E. coli*. The entrapped cells express fluorescent proteins when exposed to a molecule of interest, dependent on the concentration of this molecule. This platform is used for screening the effects of several small molecules on bacterial populations through expression of fluorescent proteins, while mitigating interference from flow-based shear stress or gradient-flattening from diffusion. A concentration-dependent fluorescent response to the interkingdom signaling molecule Autoinducer-2 is demonstrated.

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

QC+AS+BI+MN-ThP1 *In Situ* Toxic Nano-Material Sensing Method Using DNA Immobilized Quartz Crystal Microbalance, ***Kuewhan Jang***, *S. Lee, J. You, C. Park, J. Park, S. Na*, Korea University, Republic of Korea

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 where 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 sphere-plate contacts. There is an increase in resonance frequency, which can be converted to an interfacial stiffness. Interesting, the contact stiffness observed with MHz excitation was found to 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.

[1] S. Hanke, J. Petri, D. Johannsmann, *Phys. Rev. E* **2013**, *88*.

[2] P. Berthoud, T. Baumberger, Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences **1998**, 454, 1615–1634.

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 **INVITED**

Understanding interfacial phenomena has been one of the main research issues not only in semiconductors but only in life sciences. I have been trying to meet the atomic scale surface and interface analysis challenges from semiconductor industries and furthermore to extend the application scope to biomedical areas. Optical imaing has been most widely 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 raman scattering (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 biointerface 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 privides 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.

9:00am **EL+AS+BI+EM+SS-FrM3 Sum Decomposition of Mueller Matrices from Beetle Cuticles**, ***Hans Arwin***, *R. Magnusson,* Linköping University, Sweden, *E. Garcia-Caurel, A. de Martino,* LPICM-CNRS, Ecole Polytechnique, France, *K. Järrendahl,* Linköping University, Sweden, *R. Ossikovski*, LPICM-CNRS, Ecole Polytechnique, France

Spectral Mueller matrices are very rich in information about physical properties of a sample. We have recently shown that polarizing properties like ellipticity 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 $\mathbf{M}=\alpha\mathbf{M}_1+\beta\mathbf{M}_2+\gamma\mathbf{M}_3+\delta\mathbf{M}_4$, where α, β, γ and δ are eigenvalues of the covariance matrix of **M**. Two strategies for decomposition will be discussed. A Cloude decomposition will provide the eigenvalues and also the $\mathbf{M}_i$'s although the latter will contain severe noise in some spectral regions. However, a major advantage with the Cloude decomposition is that the number of nonzero eigenvalues is directly obtained, i.e. the number of contributing $\mathbf{M}_i$ matrices. In an alternative decomposition, the $\mathbf{M}_i$'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 $\mathbf{M}_D=\alpha_R\mathbf{M}_1+\beta_R\mathbf{M}_2$ with $\alpha_R+\beta_R=1$. With α_R as adjustable parameter, the Frobenius norm $||\mathbf{M}-\mathbf{M}_D||$ 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 Cloude 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 *Chrysina argenteola*, we show that more than two eigenvalues can be nonzero, especially at oblique incidence, and additional matrices are involved.

9:20am **EL+AS+BI+EM+SS-FrM4 Polymer- and Ceramic-Supported Hybrid Gas Separation Membranes Characterized by Ellipsometry**, ***Ioannis A. Mergos***, *H. Verweij*, The Ohio State University

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 CO_2 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 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), $Ce_{0.9}Gd_{0.9}O_{1.95}$ on tubular α-alumina, and successive layers of 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 of 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.

9:40am **EL+AS+BI+EM+SS-FrM5 Spectroscopic Ellipsometry Methodology for Analysis of Thin Films with Significant Surface Non-idealities: Combining Through-the-Substrate and Film-Side Measurements**, ***Jian Li***, University of Toledo, *L. Mansfield,* National Renewable Energy Laboratory, *P. Pradhan,* University of Toledo, *H. Du, S. Glenn, J. Mann, A. Norman, K. Ramanathan,* National Renewable Energy Laboratory, *R.W. Collins,* University of Toledo, *G. Teeter, D. Levi*, National Renewable Energy Laboratory

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 all interfaces between layers, at substrate/layer and layer/ambient are abrupt and smooth. Even for the simple structure of substrate/film/ambient, however, whereby the film is fabricated in a uniform process, surface non-idealities including roughness, oxides, compositional variations, or a combination of these, are inevitable. If an accurate film dielectric function is of interest, then the widely-used effective medium approximation (EMA) treatment of the surface roughness can distort the result, especially in photon energy range of strong absorption.

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 $Cu(InGa)Se_2$, $Zn(O,S)$, Cu_2ZnSnS_4, and Cu_2SnS_3 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 ε_2 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.

10:00am **EL+AS+BI+EM+SS-FrM6 A Classical Model for Depolarization through Incoherent Superposition of Dipoles Driven by Evanescent Fields**, ***Kurt Hingerl***, University Linz, Austria

A finite spectral resolution and/or an imperfectly collimated beam /and or an (areal) extended light source / and or an (areal) extended detector and/ or a sample with a varying thickness can produce depolarization effects. However, despite these experimental findings, there are to our knowledge no physical models published which trace the origin of depolarization back to the atomic properties. Therefore, we explain depolarization by the following steps:

1) A mathematical model for cross- polarization: In structured samples the Fresnel reflectances are not correct any more, they rely on homogheneity (i.e. an arbitrary shift of the sample along any surface direction). Mathematicians are aware of this and the numerical tools developed by them, e.g. finite element methods (FEM) or rigorous coupled wave analysis (RCWA), take these effects into account, when matching boundary conditions. Mathematically the Jones matrix then possesses nondiagonal elements. This cross polarization signifies the presence of a totally polarized photon state, but takes into account that p- polarized incoming light creates s- polarized outgoing and vice versa.

2) Cross- polarization then has to take into account radiating dipoles, whose radiation create the scattered cross (and later, after incoherent superposition, partially de-) polarized field. In any structured sample there are inner boundaries present and it is straightforward to show that the usual boundary conditions on the continuity of the tangential electric field and the normal of the displacement field yield inherent contradictions at these inner boundaries. In order to fulfill the boundary conditions, close to the inner boundaries **evanescent fields** must be present, which drive the atomic dipoles in ***other spatial directions than the incoming field.***

3) 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 obtained by the ***incoherent superposition*** of the single waves. The mathematical formulation is given by the Cittert- Zernike theorem (M. Born & E. Wolf, *Principles of Optics*, chapter X.9).

10:40am **EL+AS+BI+EM+SS-FrM8 The Development Of Highly-Oriented 3D Nanostructures For Use With Ultra-Thin Layer Chromatography And Ellipsometry**, ***Erika Pfaunmiller***, University of Nebraska Lincoln, *D. Peev, D. Sekora,* University of Nebraska-Lincoln, *S. Beeram,* University of Nebraska Lincoln, *C. Rice, M. Schubert, T. Hofmann, D. Hage*, University of Nebraska-Lincoln

Slanted columnar thin films based upon SiO_2 were deposited on glass substrates through the use of glancing angle deposition (GLAD). The typical length of these structures was between 500 nm and 2.5 μm. These thin films were then evaluated for use in ultra-thin layer chromatography (UTLC), which is a special type of thin layer chromatography (TLC) that uses supports that incorporate nanomaterials. In this work, a series of lipophilic dyes were analyzed through the use of both TLC and UTLC followed by detection through imaging ellipsometry. It has previously been demonstrated that changes in birefringence is seen as small organic molecules attach to some of the types of nanostructures that were used in this study. The principle behind the detection of organic chemicals that attach/adsorb onto such nanostructures is based on the variation of the optical anisotropy of highly-ordered 3D nanostructures with attached or adsorbed molecules. This causes screening of the dielectric displacement charges that are produced by the incident electromagnetic fields within the nanostructures, which can be measured as a variation of the effective birefringence of the highly-ordered 3D nanostructures. Measurement of this birefringence was done through generalized imaging ellipsometry. This combined imaging and separation approach should be useful for label-free detection in UTLC and for the chromatographic analysis of a various target compounds.

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 Ventrice, Jr., University at Albany-SUNY

8:40am **SP+AS+BI+EM+NS+SE+SS-FrM2 2013 ASSD 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. Carpick*, University of Pennsylvania

A fundamental understanding of adhesion is important for applications at all length scales, but is particularly critical in 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 ultra-strong 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 snap-in distance and the pull-off force are measured with sub-nanometer and sub-nanonewton 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 Carpick, 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 transmission electron microscopy (TEM) and Rutherford backscattering spectrometry (RBS). The sum of the Schottky barrier heights from *n*-type and *p*-type silicon substrates agree with the silicon band gap. The BEEM and BHEM spectra are fit utilizing a linearization method to the power law of the BEEM model. Spatially resolved Schottky barrier maps are generated over a 1μm x 1μm area and provide insight into the spatial homogeneity of the barrier height. Histograms of the barrier heights show a Gaussian distribution, consistent with an interface dipole model.

10:00am **SP+AS+BI+EM+NS+SE+SS-FrM6 Local Probing of Superconductivity in Half Heusler Compounds**, ***Hongwoo Baek***, NIST & Seoul National University, Republic of Korea, *J. Ha, D. Zhang,* NIST/Maryland Nano Center, University of Maryland, *Y. Nakajima, P.S. Syers, X. Wang, K. Wang, J. Paglione,* University of Maryland, *Y. Kuk,* Seoul National University, Republic of Korea, *J.A. Stroscio*, NIST

Heusler alloys have attracted interest as multifunctional experimental platforms for topological quantum phenomena ranging from magnetism to superconductivity and heavy fermion behavior. The rare-earth chalcogenide ternary half Heusler compounds were theoretically predicted to have topologically nontrivial surface states due to band inversion [1]. The lack of inversion symmetry of the crystal lattice makes unconventional pairing symmetry feasible. The superconductivity in the non-centrosymmetric half Heusler compound YPtBi was recently reported as a promising system for the investigation of topological superconductivity [2]. In this work, we use ultra low temperature scanning tunneling micro scopy to investigate the superconducting properties of the ternary half Heusler compounds YPdBi and YPtBi. Both were theoretically proposed to have topological states with different band inversion strength [1], and experimentally reported as a topological insulator [3]. Strong spin-orbit coupling and the lack of inversion symmetry present the possibility of spin-triplet superconductivity

in these materials. T he 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 B=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 YPtBi. Sequential addition of single vortices to the superconducting YPtBi 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 YPtBi.

[1] S. Chadov, X. Qi, J. Kubler, G. H. Fecher, C. Felser, and S. C. Zhang, Nat. Mater. **9**, 541 (2010).

[2] N. P. Butch, P. Syers, K. Kirshenbaum, A. P. Hope, and J. Paglione, Phys. Rev. B **84**, 220504(R) (2011).

[3] W. Wang, Y. Du, G. Xu, X. Zhang, E. Liu, Z. Liu, Y. Shi, J. Chen, G. Wu, and X. Zhang, Scientific Reports **3** (2013).

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 microcantilever 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 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.

Authors Index

Bold page numbers indicate the presenter

— K —

— L —

— M —

— N —

— O —

— P —

— Q —

— R —

— S —

— T —

— U —

— V —

— W —

— X —

— Y —

— Z —