Applied Surface Science
Room: 204 - Session AS+BI-MoM

Organic Depth Profiling

Moderator: K.G. Lloyd, DuPont, D. Moon, DGIST

8:20am **AS+BI-MoM1 Combining Gas Cluster Ion Beam (GCIB) and Angle-Resolved XPS (ARXPS) Depth-Profiling**, ***P. Cumpson***, *A. Barlow, N. Sano, J. Portoles*, Newcastle University, UK

Over the last decade there have been progressive developments in analytical sputter sources within the surface analysis community[1]. These sources (moving from monoatomic ions, to polyatomic ions, to large gas cluster ions) have progressively reduced damage, but importantly gradually reduced the thickness of the damaged layer. With argon GCIB sources at low-to-medium energy-per-atom this depth *should now be smaller than the inelastic mean free path (IMFP)* for analysis by XPS for normal monochromated lab x-ray sources. This offers the prospect of *seeing through the damage* to produce XPS depth-profiles of polymer and other organic materials that are damage-free for the first time. Angle-Resolved XPS[2] has the potential to give information at each step in the sputter-depth profile so that the undamaged profile can be faithfully reconstructed.

We have a new XPS instrument that combines an argon GCIB source with a parallel-acquisition Angle-Resolved XPS analyser, meaning that we can acquire Angle-Resolved XPS spectra simultaneously from analytical points without tilting the specimen. This combination of GCIB and parallel-acquisition ARXPS is unique as yet, so far as we know. This instrument allows us to take angle-resolved spectra at each step of a GCIB sputter-depth profile, and reconstruct the surface concentration as a function of depth. Instrument performance has been reliable and very effective since the instrument was installed in January 2013.

We have developed numerical algorithms to "unfold" damage from GCIB/ARXPS depth-profiles. These are stable and virtually automatic. X-ray damage can be an important limiting factor[3] in the case of some specific polymer types, but we present some strategies to overcome this. Otherwise the almost automatic nature of GCIB/ARXPS depth-profiling (i.e. involving no time from an expert in interpretation of damage artefacts) suggests this combination of GCIB and ARXPS is a powerful technique for the surface analysis community, especially where (such as in organic electronics) electronic information is sought as function of depth, or cases where we start with very little *a priori* certainty about the structure of samples (as is often the case in analysing biological materials).

[1] S. Rabbani, A. M. Barber, J. S. Fletcher, N. P. Lockyer, and J. C. Vickerman, Anal. Chem. 83, 3793 (2011).

[2] PJ Cumpson, J Elec spectrosc 73 (1), 25-52 (1995)

[3] X-ray enhanced sputter rates in argon cluster ion sputter-depth profiling of polymers. P. J. Cumpson, J. F. Portoles, N. Sano and A. J. Barlow, J. Vac. Sci. Technol. B 31, 021208 (2013)

8:40am **AS+BI-MoM2 XPS Analysis of Oxygen Plasma Modified Polyethylene Surfaces**, ***S.S. Alnabulsi***, Physical Electronics Inc., *N. De Geyter, R. Morent,* Ghent University, Belgium, *J.F. Moulder*, Physical Electronics Inc.

Plasma modification of polymers is of great interest for surface preparation to enhance the covalent binding of functional groups and the surface adhesion in biomedical applications. The depth of the plasma treatment is expected to be limited to the top few nanometers, and in this this study, we are investigating the extent of oxygen incorporation through plasma surface modification of a polyethylene surface while varying treatment parameters, and examining the effects of aging on the stability of the modified layer.

Obtaining quantitative chemical state information of the extent of the plasma modification as a function of depth and determining the extent of the depletion region is accomplished through the application of XPS depth profiling utilizing two complimentary methods; the first is with the application of an angle dependent profile to probe the outer most layers of the modified surface, and the second is a sputter depth profile with C_{60} cluster ion beam.

We will present complimentary XPS results of angle dependent profiles and C_{60} sputter depth profile analyses of plasma modified polyethylene to reveal changes in the composition of the modified surface layers, which may explain the effects of varying the plasma treatment parameters, and the effects of sample aging on the shelf life of these modified polymers.

9:00am **AS+BI-MoM3 XPS Valence Band Profiling of Polymer Mixtures with Argon Cluster Ions**, *P. Mack*, ***A.E. Wright***, Thermo Fisher Scientific, UK

Modern food packaging materials can be complex mixtures of polymers, with a wide range of surface properties, compositions and structures. X-ray Photoelectron Spectroscopy (XPS) is typically the technique of choice for analyzing polymeric surfaces, combining chemical selectivity and surface specificity. Core level XPS spectroscopy, however, is not always sensitive to compositional changes in complex mixtures of polymers. A commonly cited example of this would be in the analysis of blends of polypropylene and polyethylene. Each of the individual polymers in this case has an almost identical C1s spectrum, meaning the polymeric mixtures cannot be quantified using the core level data.

The valence region of the XPS spectrum, however, has been shown to be sensitive to compositional changes in polymeric mixtures even when the core level spectra are not. The XPS valence band of polyethylene and polypropylene, for example, are significantly different and using reference data for each of the individual polymers, it is possible to quantify mixtures of the two.

There has also been an increasing requirement for compositional profiling of these complex materials. Profiling with monatomic argon can result in a high degree of chemical modification during the acquisition of depth profiles for organic materials, but it has been shown recently that the use of argon cluster beams for depth profiling can preserve chemical information during analysis of organic materials. This talk will present data from cluster profiling studies of polymer blends, using XPS valence band analysis to quantify the polymeric mixtures during the profile.

9:20am **AS+BI-MoM4 Successful XPS Sputter Depth Profiling of Organic Materials Using Massive Argon Cluster Ions**, ***S.J. Hutton***, Kratos Analytical Limited, UK, *J. Walton,* The University of Manchester, UK, *W. Boxford, C.J. Blomfield, J.D.P. Counsell, S.C. Page*, Kratos Analytical Limited, UK

Several XPS vendors currently offer massive Argon gas cluster ion sources as accessories for sputter depth profiling of organic materials. These sources utilise Argon cluster ions formed via adiabatic isentropic expansion of Argon gas into a vacuum followed by subsequent electron impact ionisation and cluster size selection. In ideal cases the aforementioned massive cluster ions efficiently sputter the surface of organic materials revealing undamaged subsurface structure for analysis.

Advanced software controlled ion sources and flexible sample handing equipment allow a wide range of experimental conditions to be routinely employed during sputter depth profiling with these massive Argon clusters. In this study we investigate these parameters including: incident ion energy; cluster size distribution; ion angle of incidence; and sample condition (temperature, rotation). A range of organic materials are analysed and optimum sputter depth profiling conditions determined.

9:40am **AS+BI-MoM5 3D Characterization of Multi-Layer Polymer Films by XPS and TOF-SIMS**, *S. Iida, T. Miyayama,* ULVAC-PHI, Inc., Japan, *G.L. Fisher, J.S. Hammond,* ***S.R. Bryan***, Physical Electronics Inc.

The recent introduction of Gas Cluster Ion Beams (GCIB) and FIB-TOF has provided new possibilities for 3D characterization of organic materials. The use of GCIB as a sputter beam for both XPS and TOF-SIMS has made it possible to acquire molecular depth profiles on a wide variety of polymers. The purpose of this study was to compare XPS and TOF-SIMS depth profiling to FIB-TOF analysis of a model Polystyrene (PS)/PS+Nylon/Nylon/PS+Nylon/PS multi-layer structure. Total thickness of the muli-layer stack is 10 um. XPS depth profiling provided quantitative analysis that could be used to calibrate the TOF-SIMS data. Both TOF-SIMS depth profiling and FIB-TOF can provide 3D characterization of the polymer stack. The TOF-SIMS data provided imaging of the heterogeneous distributions found in each of the PS+Nylon layers as well as trace molecular components found throughout the multi-layer stack. Advantages and disadvantages of both approaches to 3D analysis will be discussed using data from this polymer multi-layer model system.

10:00am **AS+BI-MoM6 *In Situ* TOF-SIMS and SFM Measurements Providing Real 3D Chemical Information**, ***E. Niehuis***, *S. Kayser, R. Möllers,* ION-TOF GmbH, Germany, *L. Bernard, H.-J. Hug,* EMPA, Switzerland, *N. Havercroft,* ION-TOF USA, Inc., *R. Dianoux, A. Scheidemann*, NanoScan AG, Switzerland

Advances in analytical instrumentation and nanometrology have been the key to the remarkable progress in nanoscience and nanotechnology research over the last two decades. Detailed knowledge of the chemical composition,

physical properties and the three dimensional structure of materials and devices at the nanometer scale is required in all phases of the development from exploratory research to concept and prototyping and finally manufacturing.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a very sensitive surface analytical technique. It provides detailed elemental and molecular information about surfaces, thin layers, interfaces, and full three-dimensional analysis of the sample.

In recent years bismuth clusters have become the standard analysis species for all imaging applications providing a lateral resolution of down to 80 nm. 3D chemical information can be derived by a well-controlled removal of surface layers with an additional sputter beam in a so-called dual beam experiment. Inherent to all 3D TOF-SIMS data is a z-axis with a native time scale instead of a length scale. A starting topography of the initial sample surface as well as an evolving topography due to different erosions rates of the compounds cannot be identified by the technique and yields to relevant distortions.

Scanning force microscopy (SFM), has become the most versatile scanning probe microscopy (SPM) technique since its first application in 1986. In a scanning force microscope, a microscopic tip is scanned over the surface of interest and probes the local properties at each pixel of the scan region. A SFM cannot only map topography up to atomic resolution; it can also map other sample properties with nanometer scale resolution such as local mechanical properties, materials contrast, or electric and magnetic stray fields emanating from the surface.

We have developed a TOF-SIMS / SFM instrument which combines both complementary techniques in a single UHV chamber. The core piece of the new instrument is a high precision, five axes piezo stage which allows fast and accurate navigation between the TOF-SIMS and the SFM analysis position. The combination makes it possible to acquire SFM data before, after and in between TOF-SIMS acquisitions at exactly the same sample position.

In this paper we will present first measurements illustrating the strength of this novel instrument and its potential for a wide range of applications including sputter induced effects on the surface morphology of organic surfaces.

10:40am **AS+BI-MoM8 Time of Flight Secondary Ion Mass Spectroscopy (ToF SIMS) Analysis of Stress Tolerant Polymer (STP) in GenGard Corrosion Inhibitors**, ***G. Zorn***, *M. Karadge, M.M. Morra,* GE Global Research, *J. Davis, C.C. Pierce, J.I. Melzer*, GE Power & Water

GE Power & Water GenGard technology is GE's most advanced and effective water treatment technology for open recirculating cooling systems. It can be applied across a broad pH spectrum and provide superior results, even under the most stressed system conditions. The patented GenGard technology includes a new Stress Tolerant Polymer (STP) in combination with phosphate-based steel corrosion inhibitors. The GenGard technology, when used, develops complex multilayered structures that incorporate metal, ceramic and polymer, where the STP is designed to maintain phosphate-based corrosion inhibitors' solubility. For optimal performance it is important to understand the structure, morphology and composition of different layers. However, characterizing these nano scale films is very challenging, as they can be sensitive to preparation technique and damage. Moreover, surface roughness and homogeneity of the layers should be considered.

This work is focused on the ToF SIMS study of the multilayered structures formed by the GenGard technology, with an emphasis on the STP analysis and its distribution within the inhibition layers. ToF-SIMS is capable of high detection sensitivity (ppb), very high surface specificity (analysis of the top 1-3 surface layers during date acquisition, high mass resolution (Δm/m greater than 8000), and is able to detect high mass molecular fragments associated with the STP. ToF SIMS allows rapid data collection while analyzing through multilayers, and provides high interfacial resolution during a depth profile measurement.

ToF SIMS depth profiling of the structures formed by the GenGard technology showed a calcium phosphate / iron oxide two layer structures on the base metal. This structure was further confirmed by Transmission Electron Microscopy (TEM) equipped with Energy Dispersive X-Ray Spectrometer (EDS). The STP that is added in ppm levels was identified in the ToF-SIMS by three high mass $Na_xS_yO_z$ fragments at m/z=229,245 and 261 amu. In order to eliminate the possibility that these fragments are associated with surface contamination, Ion Chromatography (IC) was performed. After identifying the STP characteristic tags, ToF SIMS depth profiling of the inhibition layers allows showing that the STP is incorporated within the entire inhibition layers at the initial steps (after 7 days) but later it starts to migrate to the surfaces of these films as they grow with time. This ToF SIMS study combined with TEM and IC provides a detailed picture of the complex structures and compositions as well as the kinetic behavior of the inhibition films formed by the GenGard technology.

11:00am **AS+BI-MoM9 Argon Gas Cluster Beam Etching of Organic Contaminants on Graphene and HOPG**, ***BJ. Tyler***, *A.J. Pollard, I.S. Gilmore*, National Physical Laboratory, UK

Under ambient conditions, the surface of graphene is contaminated with a range of organic compounds. These compounds include both those that derive from the production of the graphene, such as photo-resists and transfer agents, and adventitious organic compounds that adsorb rapidly to the high energy graphene surface. The ability to remove and control this contamination layer without damaging the graphene is crucial to reproducible production of graphene devices as well as in fundamental studies of graphene properties. In this study, we have investigated cleaning of HOPG and graphene surfaces via heating in vacuum and sputtering with Argon Gas Clusters. Common adventitious organic contaminants have been identified via temperature programmed SIMS experiments and include fatty acids and their fatty acid amides, as well as PAHs and siloxanes. While contamination with siloxanes can be avoided with careful handling, adsorption of fatty acids and amides is virtually instantaneous upon exposure to the ambient environment. Damage to the graphene layer via the sputtering process has been assessed via micro-Raman analysis. Formation of defects due to sputtering with Argon Gas Clusters is dependent on the cluster size, impact energy and ion fluence. An impact energy of less than 1eV per atom in the cluster is needed to minimize defect formation. Optimized conditions for sputter profiling these organic overlayers without damaging the underlying graphene will be presented.

11:20am **AS+BI-MoM10 Why is Low Energy Cesium so Efficient for Depth-profiling Organics?**, ***L. Houssiau***, University of Namur, Belgium **INVITED**

Organic materials are known to be very sensitive to ion bombardment, mostly owing to free radical creation upon etching, leading to many chemical reactions like hydrogen abstraction, double bond creation and crosslinking. Most organics eventually degrade into a graphitized material, with no memory left of the initial material's chemistry. However, this picture has dramatically evolved over the last decade thanks to breakthrough developments in the field of molecular depth profiling. It started with the use of polyatomic ion sources (SF_5^+, C_{60}^+), followed by massive Ar_n^+ clusters which are now considered as standards for molecular depth profiling. Those cluster sources exhibit a sputtering yield high enough to sputter molecular damages away. Our group has followed a thoroughly different approach since 2007, when we showed that, surprisingly, low energy (~250 eV) Cs^+ ions could also be used to depth profile polymers. We have extended the study to many different organic materials, including amino acid thin films, analyzed in the energy range 150-1000 eV. So far, it appears that most organics are amenable to depth-profiling with this method, making it a complementary approach to cluster ion beams. We will review our understanding on how low energy Cs^+ ions prevent material degradation. Cs^+ ions are neutralized as soon as they hit the surface, for electrostatic reasons, leaving implanted Cs atoms in the subsurface region. Cs being an extremely reactive element quickly reacts with free radicals generated by ion impact, preventing cross-linking reactions, thus allowing molecular depth profiling. This reaction goes along with a strong negative ionization, as an electron is transferred from the alkali to the molecule. Indeed, negative molecular ion detection in ToF-SIMS experiments is much increased with respect to inert ions. Our model is supported by XPS data, showing changes in the charge state of various molecules (amino acids, polymers) irradiated with Cs^+ ions. Moreover, the existence of neutral cesium at the surface was detected by optical emission spectroscopy measurements. We will present our most recent data on Phenylalanine delta layers embedded in a Tyrosine matrix, on which a depth resolution below 5 nm was observed. We will also discuss the decisive influence of the analysis beam (i.e. Ga^+ or Bi_3^+) in a ToF-SIMS dual beam experiment. Besides its fundamental interest, low energy Cs^+ sputtering appears to be an efficient tool to depth profile both organics and inorganics. Its major assets are a high negative ion signal combined with an excellent depth resolution.

Biomolecules at Aqueous Interfaces Focus Topic
Room: 203 A - Session BA+AI+AS+BI+IS+NL-MoM

Biomolecules at Aqueous Interfaces
Moderator: P. Koelsch, University of Washington

8:20am **BA+AI+AS+BI+IS+NL-MoM1 Selected Studies of Biomolecular Interactions**, ***K.B. Eisenthal***, *B. Doughty, Y. Rao, S.M. Kazer, S.J.J. Kwok, N.T. Turro*, Columbia University **INVITED**

The work reported here utilizes a sensitive method for the investigation of biomolecular interactions that has the important characteristic of not requiring chemical labels, e.g. fluorophores, nor invasive detection methods. The surface selective second order spectroscopies, second harmonic, SHG, and sum frequency generation, SFG, allow one to probe equilibrium properties and time dependent changes in the electronic and vibrational structure of molecules located at interfaces. In addition they have the special feature of being able to monitor changes in the electrical charge of the interacting molecules. 1) A new way is presented to measure the binding constants of molecules, e.g. drugs and proteins, with DNA tethered to colloidal microparticles suspended in aqueous solution. 2) Time resolved second harmonic generation was used to observe the binding of an enzyme to its recognition site on DNA, followed by the cleaving of DNA into a small and a large fragment, and the subsequent DNA rehybridization dynamics. 3) The relative orientation of two molecules bound to DNA is manipulated by changing the number of nucleotide base pairs separating them. The interference between the SH electric fields generated by the pair of molecules is modulated because their relative orientation changes as the number of nucleotide base pairs separating them is changed. With this method we have a new way to probe structural changes in DNA due to the binding **of** biomolecules to it.

9:00am **BA+AI+AS+BI+IS+NL-MoM3 Probing Nanoparticle-lipid Bilayer Interactions with Nonlinear Optics**, ***F. Geiger***, Northwestern University **INVITED**

The interaction of engineered nanoparticles with biological membranes is an important and necessary first step for cellular uptake. Here, we probe this interaction by applying second harmonic and vibrational sum frequency generation as well as the Eisenthal chi(3) method to supported bilayer-based model systems as well as shewanella and daphnia magna, chosen as important biological endpoints, exposed to 4 nm sized noble metal nanoparticles surrounded by negatively and positively charged ligands. Our studies are complemented by a plethora of supporting experiments based on quartz crystal microbalance, zeta potential, and related experiments. We find that Coulomb's law dictates much of the interactions in the particular systems studied here.

9:40am **BA+AI+AS+BI+IS+NL-MoM5 Characterizing the Protein-Surface Interactions that Control Diatom Biomineralization**, ***J.E. Baio***, Oregon State University, *M. Bonn, T. Weidner*, Max Planck Institute for Polymer Research, Germany

The assembly of mineralized tissues can be initiated and controlled by proteins. One such system, is the formation of silica-based cell walls in marine, single celled organisms, where biomineralization is regulated by protein−mineral interactions. The diatom species *Cylindrotheca fusiformis* assembles supramolecular silica structures via proteins called sillafins. In a silicic acid solution, specific repeat units within this protein, SSKKSGSYSGSKGSKRRIL (R5), induce the formation of silica-protein composite nanoparticles. The protein−surface interaction that drives self-assembly is likely controlled by both the secondary structural motifs of the protein and specific contacts between the surface atoms and key protein side chains. In this study, we characterized the R5-SiO_2 interactions that drive this self-assembly process by both near edge x-ray absorption fine structure (NEXAFS) spectroscopy and *in situ* sum frequency generation (SFG) spectroscopy. Two peaks within the amide I vibrational band of the SFG spectra, 1640 and 1670 cm^{-1}, indicate that the R5 peptide retains a beta sheet conformation when interacting with SiO_2. Expanding upon this characterization of secondary structure, the introduction of isotopic labeled amino acids within the peptide allowed us to probe the orientations of individual side chains by SFG. This SFG characterization was complemented by the observed polarization dependence of the NEXAFS C1s to π^* transition which provided details of the binding geometry of the single tyrosine within R5.

10:00am **BA+AI+AS+BI+IS+NL-MoM6 Probing the Effects of Different Ions on the Formation of Microstructure Within Collagen Hydrogels by Second Harmonic Generation (SHG) Microscopy**, ***X. Lang***, *J.G. Lyubovitsky*, University of California, Riverside

In this study we aimed to explore the nucleation, assembly and the 3-D microstructure of collagen hydrogels *in situ* with second harmonic generation (SHG) microscopy. Transmission electron microscopy (TEM) and optical density (OD) were carried out as well in order to complement the SHG measurements. The goal was to generate the knowledge to accelerate rational design of collagen-based biomedical products. In this work, we employed 0, 150, 300, 600, 900 mM NaCl concentrations and in a separate experiment 0, 5, 10, 20, 50, 75, 100, 150, 300 mM Na_2SO_4 concentrations of salts needed for the assembly of collagen hydrogels. Specifically, we characterized collagen hydrogels prepared from 2 g/l and 4 g/l initial collagen concentrations as well as several incubation temperatures. For samples incubated with NaCl, incubation under the room temperature (RT) and 27°C gave similar OD values. These OD values were higher than the OD values for 37°C incubated samples. Delay time became shorter upon elevating the polymerization temperature. For samples incubated with Na_2SO_4, there were two regimes for collagen polymerization, Na_2SO_4 concentration 5 mM – 50 mM and 100 mM -300 mM. Fibers were longer when NaCl concentration was 150-600 mM compared to 0 and 900 mM NaCl for both collagen concentrations under RT, 27°C and 37°C. In general, fibers were small when incubated at 37°C compared to fibers formed under RT and 27°C. TEM measurement showed that there were collagen fibers with a characteristic striation structure in all collagen and NaCl concentrations. The fibrils exhibited a twisted morphology in 2 g/l collagen hydrogels.

10:40am **BA+AI+AS+BI+IS+NL-MoM8 Sum Frequency Generation (SFG) Vibrational Spectroscopy Studies of Molecules at Solid-Liquid and Solid-Gas Interfaces**, ***G.A. Somorjai***, University of California, Berkeley and Lawrence Berkeley National Laboratory, *X. Cai*, Lawrence Berkeley National Laboratory **INVITED**

Construction of a femtosecond broad-band laser enables us to simultaneously monitor the CH and CO vibrational SFG spectra, thus allowing more actual characterization of reaction intermediates at solid-liquid and solid-gas interfaces. Using a picosecond laser we compare the spectroscopy using these two different laser systems and they will be discussed in some detail. In addition, sum frequency generation vibrational spectroscopy, high-pressure scanning tunneling microscopy and ambient-pressure X-ray photoelectron spectroscopy as well as other synchrotron-based techniques (X-ray adsorption) that enable the investigation of surfaces under reaction conditions on the atomic and molecular level will be reviewed.

We investigate solid-liquid and solid-solid interfaces (buried interfaces) as they adsorb and react with diatomic and organic molecules in dynamic state at various pressures and temperatures.

11:20am **BA+AI+AS+BI+IS+NL-MoM10 A Molecular View of Water Interacting with Climate-active Ice Nucleating Proteins**, *R. Pandey*, Max Planck Institute for Polymer Research, Germany, *J. Fröhlich, U. Pöschl*, Max Planck Institute for Chemistry, Germany, *M. Bonn*, ***T. Weidner***, Max Planck Institute for Polymer Research, Germany

Specific bacteria, such as *Pseudomonas syringae*, effectively attack plants by using ice-nucleating proteins anchored to their outer cell surfaces. Ice nucleating proteins promote the local crystallization of ice at temperatures that would otherwise not allow ice formation. The frost damage caused by ice crystals then facilitates bacterial invasion of the affected plants. Ice nucleating proteins not only play an important role for agriculture, but are also very important for atmospheric processes: airborne ice-nucleating proteins have been shown to be among the most effective promoters of ice particle formation in the atmosphere. A recent survey of microorganisms in the troposphere biome by NASA has discovered massive emissions of biogenic ice nucleators from large forest areas like the amazon, which likely change precipitation patterns and may affect the global climate. To understand biogenic ice formation, a detailed molecular level picture of the mechanism by which ice-nucleating proteins interact with water molecules is important. Sum frequency generation (SFG) spectroscopy – owing to its inherent interface sensitivity – is ideally suited to determine the structure and dynamics of water molecules at interfaces. We have investigated the interaction a monolayer of the ice-nucleating protein inaZ with water using static and time-resolved SFG spectroscopy. When cooling the sample from room temperature to near-freezing temperatures (~5°C for D_2O), inaZ significantly increases the structural order of water molecules in contact with inaZ proteins. This effect was not observed for liquid water surfaces without the protein or for protein monolayers which are not ice nucleators. SFG spectra in the CH and the amide I region also indicated a change of protein structure near the nucleation temperature. Femtosecond, time-resolved 2-dimensional SFG spectroscopy is used to quantify the

heterogeneity of protein-bound water molecules and their structural dynamics.

Biomaterial Interfaces
Room: 201 B - Session BI+AS+IS+NL-MoM

Surfaces to Control Cell Response
Moderator: H.E. Canavan, University of New Mexico

8:20am **BI+AS+IS+NL-MoM1 Modulation of Cell Behaviour using Self–assembled Binary Colloidal Crystals**, ***P.Y. Wang***, *P. Kingshott*, Swinburne University of Technology, Australia

The control of cell behaviour on surfaces is the key to a broad range of biomedical applications. Biomaterial surfaces with tuneable surface topographies and chemistries can profoundly influence the development of advanced biomaterials used in applications including tissue engineering and regenerative medicine. Recently, we developed an elaborate and feasible method to display an ordered surface topography with tuneable surface chemistry using binary colloidal crystal particles. Using this binary colloidal system, various combinations of particle size and surface chemistry can be readily employed. In this study, two combinations of binary colloidal crystals, i.e. PS-COOH (2 μm)/PMMA (0.4 μm) and SiO_2 (2 μm)/PMMA (0.4 μm) were assembled on ozone-treated silicon wafers. The preliminary results of cell attachment and morphology of L929 fibroblasts and MG63 osteoblasts were studied after 24h.

In general, cells had a small projection area rather than fully spread morphology on the crystal surfaces compared with the flat control. Fibroblasts have abundance of cell protrusions called filopodia which can be observed using scanning electron microscopy (SEM), whilst osteoblasts don't have. Fibroblasts had long and thin extended filopodia on the PS/PMMA crystal surfaces, whilst they had short and thick filopodia on the SiO_2/PMMA crystal surfaces. Regarding the surface chemistry, both SiO_2 and PMMA particles were not as favourable as the PS-COOH particles for fibroblasts attachment, and resulted in the cell projection area on the PS/PMMA being larger compared to the SiO_2/PMMA crystal surfaces. On the contrary, the cell projection area of osteoblasts didn't have significant differences between these two crystal surfaces. After fibronectin coating, cell projection area of osteoblasts on SiO_2/PMMA crystal surfaces increased significantly, whilst fibroblasts didn't, suggesting that different cell types respond to surfaces differently.

These results show for the first time that cell-substrate interactions can be easily controlled by precise positioning of different particles with various sizes and chemistries. The present results will help gain a more thorough understanding of cell-material interactions benefiting the development of advanced biomaterials and materials for tissue engineering.

8:40am **BI+AS+IS+NL-MoM2 Achieving Differential Cell Adhesion with Novel Polymer Surfaces Identified using Microarrays**, ***F.A. Simoes***, *C. Alexander, G. Mantovani, L. Buttery, M.R. Alexander*, University of Nottingham, UK

Stem cells have the ability to repair, replace or regenerate tissues. As a result their potential for regenerative medicine is vast. The processing of cells for therapeutic use and clinical diagnostics will rely on cell sorting steps to ensure a homogeneous population is obtained.[1]

Several techniques exist to achieve this, which rely on the physical properties of cells but tend to provide poor specificity.[2-4] Fluorescence Activated Cell Sorting (FACS) and Magnetic-Activated Cell Sorting (MACS) rely on specific biomarkers. However cells require labelling and label removal steps, which can affect the phenotype.[5]

There is a need for a fully synthetic, inexpensive, label-free separation system, capable of sorting cells with minimum manipulation. In order to generate robust surfaces for such a system, we have developed a method to immobilize thiol-functionalised materials to a polymer substrate using thiol-ene "click" chemistry in a high throughput format. Microarrays of these functionalised polymers comprising of 6 replicates, are fabricated using pin printing to generate a combinatorial library of materials. A mixture of differentiated cells derived from mouse embryoid bodies are then seeded onto the arrays.

Immunohistochemistry techniques are employed to track the differentiation of cells into different lineages, thus enabling the visualisation of multiple cell lines. These techniques also allow for the high throughput quantification of attachment by the means of automatic fluorescence microscopy.

Surface characterisation of the "click" immobilization procedure is performed by X-Ray Photoelectron Spectroscopy. In contrast the characterisation of microarrayed materials is performed using Time of Flight - Secondary ion Mass Spectrometry, which is followed by the ranking of materials using Partial Least Square (PLS) regression analysis. This process allows for the correlation of cell attachment with key molecular ions generated from each material by mass spectrometry.

Successful materials that selectively induce cell attachment are identified and investigated further. This is the first step in the generation of new surface-based devices that have the capacity to be fully synthetic, selective, inexpensive and disposable.[6]

1. McIntyre C. *et al*., *Bioprocess International*, 2010, 44-53.

2. Chabert M. and Viovy J., *PNAS*, 2008, **105**, 3191-3196.

3. Shim S. *et al*., *Integrative Biology*, 2011, **3**, 850-862.

4. Kose A. R. *et al*., *PNAS*, 2009, **106**, 21478-21483.

5. Bulte J. W. M. *et al*., *Blood*, 2004, **104**, 3410-3413.

6. Singh A. *et al*., *Nature Methods*, 2013, **10**, 438-444

9:00am **BI+AS+IS+NL-MoM3 Interaction of Hematopoietic and Leukemic Cells with their Microenvironment**, ***A. Rosenhahn***, Ruhr-University Bochum, Germany, *M. Hanke, C. Christophis,* Karlsruhe Institute of Technology, Germany, *I. Taubert, N. Baran, P. Wuchter, A.D. Ho*, University of Heidelberg, Germany

Especially for leukemic and haematopoietic cells, the interaction with their microenvironment is of upmost importance for extravasation and homing. One key mechanism is the interaction of the CD44 receptor with extracellular hyaluronan (HA) binding motifs. To quantitatively assess the interaction, a microfluidic experiment has been developed that allows studying the interaction of cells with interfaces under well-defined flow conditions [1]. Shear flow activated catch bond interaction is well characterized for selectin mediated extravasation of leukocytes [2]. We recently found that also the CD44 interaction with HA requires a minimum shear stress to become activated and enable cells to roll on HA surfaces [3]. Similar critical shear values were found for rolling on mesenchymal stroma cells, which are present in the bone marrow niche creating the microenvironment required for haematopoietic stem cell renewal. Interestingly not only hematopoietic stem cells but also acute leukemic blasts show a shear flow induced rolling. The proportion of rolling cells will be discussed on the basis of the pathogenesis of the disease.

[1] C. Christophis, M. Grunze, A. Rosenhahn, PCCP 2010, 12, 4498.

[2] E.B. Finger, K.D. Puri, R. Alon, M.B. Lawrence, U.H. von Andrian, T.A. Springer, Nature 1996, 379, 266

[3] C. Christophis, I. Taubert, G. Meseck, M. Schubert, M. Grunze, A. D. Ho, A. Rosenhahn, Biophys. J. 2011, 101, 585.

9:20am **BI+AS+IS+NL-MoM4 The Creation of Polymeric Biointerfaces using Non-Contact Dispensing Technology**, ***C. Dufresne***, Scienion

Polymeric surfaces of varied composition have been created in high density microarray formats. These patterned surfaces have been used to study a number of biointerface processes such as stem cell differentiation, and bacterial adhesion. Scienion offers non-contact picoliter dispensing technology that enables the creation of such surfaces. The inert glass capillaries allow for the use of a wide range of chemical reagents. Precision positioning enables drop-on-drop dispensing and mixing. Image analysis of the substrates in turns makes it possible to accurately dispense the materials onto almost any surface. This presentation will cover how Scienion technology is implemented for the production of polymeric surfaces.

9:40am **BI+AS+IS+NL-MoM5 The Role of Cell-Substrate Interactions on Cell Stiffness and Cell Volume**, ***D.A. Weitz***, Harvard University **INVITED**

Cell stiffness is often observed correlate with the stiffness of the substrate on which the cells are grown. This talk will present data which suggest that cell-substrate interactions are more diverse, and depend as well on the adhesion area. It will discuss the impact of the substrate on cell volume and the consequences of this on cell stiffness. The data presented will suggest that cell volume is a control for cell stiffness.

10:40am **BI+AS+IS+NL-MoM8 Quantitative, Predictive Models of Adhesion of Cells to Polymers**, ***V.C. Epa***, *D.A. Winkler,* CSIRO Materials Science & Engineering, Australia, *A.L. Hook, C. Chang, J. Yang,* University of Nottingham, UK, *R. Langer, D.G. Anderson,* MIT, *P. Williams, M.C. Davies, M.R. Alexander*, University of Nottingham, UK

Designing materials to control biology is an intense focus of biomaterials and regenerative medicine research. Discovering and designing materials with appropriate biological compatibility or active control of cells, tissues,

or pathogens is being increasingly undertaken using high throughput synthesis and assessment methods.

In particular, culture of multipotent cells such as stem cells is a major research focus in regenerative medicine. Much research effort is focused on designing chemically defined, serum-free, feeder-free synthetic substrates and media to support robust self-renewal of pluripotent cells. Changes in cellular properties such as adhesion, morphology, motility, gene expression and differentiation are influenced by surface properties of the materials on which cells have been cultured. Similarly, designing new materials to control the growth of pathogens on implantable and indwelling devices such as pacemakers, and catheters, is critical given the high level of device-centred infections.

We report a relatively simple but powerful machine-learning method of generating models that link microscopic or molecular properties of polymers or other materials to their biological effects. We illustrate the potential of these platform modelling methods by developing the first robust, predictive, quantitative, and purely computational models of adhesion of human embryonic stem cell embryoid bodies, and three clinically important pathogens, *Staphylococcus aureus*, *Pseudomonas aeruginosa*, and uropathogenic *Escherichia coli*, to the surfaces of 496 polymers.

11:00am **BI+AS+IS+NL-MoM9 Smart Surfaces for Studies of Real-Time Dynamic Cell Behavior**, ***M.N. Yousaf***, York University, Canada

Active migration, local tissue invasion and seeding of distant metastases are all characteristics of malignant cells. These complex cellular events require the integration of information derived from soluble growth factors with positional information gained from interactions with the extracellular matrix and with other cells. The biochemical events of the signaling cascades occur in a spatially and temporally coordinated manner that then dynamically shape the cytoskeleton in specific sub-cellular regions. Therefore cell migration and invasion involve a precise but constantly changing subcellular nano-architecture. To fully understand the complex signaling and cytoskeletal aspects of the cellular nano-architecture during migration requires a multidisciplinary coordinated effort. The long-term goal of this research program is to develop new surface chemistry and cell biological tools to generate a class of tailored dynamic nanopatterned substrates for a variety of cell adhesion and migration experiments. The combined application of dynamic smart substrates, molecular surface gradients and in vivo biosensors will potentially allow for the analysis and quantitation of the events of cell migration at each step from initial engagement with extracellular matrix ligands, to localized activation of signaling proteins, to organization and activation of the cytoskeleton, to overall movement of the cell.

11:20am **BI+AS+IS+NL-MoM10 What Makes the Heart Grow Fonder? Chemically Diverse Polyacrylate and Polyacrylamide Surfaces for Human Cardiomyocyte Culture and Their Effect on Phenotype**, ***A.K. Patel***, University of Nottingham, UK, *D.G. Anderson, R. Langer,* Massachusetts Institute of Technology, *M.C. Davies, M.R. Alexander, C. Denning*, University of Nottingham, UK

Human pluripotent stem cell (hPSC) derived cardiomyocytes hold the potential to strengthen pharmaceutical toxicity testing and to provide disease models for development of treatment targets1. The maturation and maintenance of the cardiomyocyte phenotype may be controlled by the manipulation of the substrate supporting the cells2. However, the surfaces currently in use still fall short of producing cardiomyocytes of adult maturity. Standard culture-ware requires coating with biological substrates such as fibronectin which can be expensive and subject to poor reproducibility due to batch variation. We are exploring an alternative, combinatorial materials high throughput screening approach3 to identify novel materials that can improve cardiomyocyte culture. Polymer microarrays comprising of 6 replicates of 116 acrylates and acrylamides are fabricated using contact printing. Cardiomyocytes derived from the HUES7 human stem cell line are seeded onto the arrays. Immunostaining of nuclei (DAPI) and the cardiomyocyte specific motor protein, sarcomeric alpha actinin is performed to visually estimate cell function and maturity and enable quantification of cell attachment in a high throughput manner using automated fluorescence microscopy and image analysis software. Surface characterisation of the arrays is performed using time of flight secondary ion mass spectrometry. Partial least squares (PLS) regression analysis allows for correlation of cell attachment with key molecular ions identified from mass spectrometry4.

Successful monomers that permit cardiomyocyte attachment, spreading and contraction are identified from the first generation homopolymer microarray and are mixed pair-wise to form second generation microarrays. This diverse library of copolymers enables unique combinations of chemical moieties to be investigated. Hit monomers and combinations identified to be synergistic can be analysed for their effect on cardiomyocyte function including electrophysiology measured by patch clamping, myofibril alignment and gene expression.

The lead materials generated by this approach are the first step in a discovery process for novel synthetic biomaterials capable of enhancing the culture of cardiomyocytes to move towards more reproducible, economical and defined conditions.

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1. Matsa E. et al. European Heart Journal. 2011;32(8):952-62

2. Engler A. et al.The Journal of Cell Biology. 2004;166(6):877–887

3. Hook A. et al. Biomaterials. 2010;31(2):187–198

4. Yang J. et al.Biomaterials. 2010;31(34): 8827–8838

11:40am **BI+AS+IS+NL-MoM11 Selectivity in Platelet Activation by the Titania Surface: A Model System for In Vitro Modulation of Platelet Activity**, *S. Gupta,* CIC biomaGUNE, Spain, ***I. Reviakine***, Karlsruhe Institute of Technology, Germany

Platelet are anuclear cell fragments circulating in blood. Their major function is haemostasis: they catalyze the formation of the fibrin clot that stops the bleeding. Recently it was shown that they have a multitude of other functions in processes such as the immune response, inflammation, angiogenesis, implant rejection or integration.

Platelets circulate in the blood in a quiescent form. They become activated at wound sites, implant surfaces, or through the action of soluble agonists secreted by activated platelets or produced in the blood as a result of the clotting process. Activated platelets express on their surface a variety of protein and lipid receptors that catalyze the clotting process, interact with other platelets, leukocytes, and endothelial cells, and adhere to the extracellular matrix exposed at the wound sites. The also secrete a variety of active substances, including growth factors, that are stored inside special granules within the platelets.

Recently discovered diversity of platelet functions implies a tight regulation of the activation processes. Indeed, there is evidence to suggest that platelet activation is a selective process with a spectrum of activated states, rather than a two-state process involving quiescent vs. pro-coagulant platelets. In this context, we have previously shown that platelet activation profile on TiO_2 depends on the surface-bound Ca. Here, we measure intracellular calcium currents in surface-adsorbed platelets in order to understand how this manifestation of platelet activation selectivity is related to the internal signaling pathways. Such an understanding is a prerequisite for designing new, platelet-based approaches to the treatment of haemostatic and inflammation-based disorders, to enhancing implant integration and wound repair, and to tissue engineering applications.

Nanometer-scale Science and Technology
Room: 203 B - Session NS+BI+EM-MoM

Nanophotonics and Plasmonics
Moderator: D. Wei, University of Florida

9:00am **NS+BI+EM-MoM3 Predetermining Paths of Nanoscale Crack by Local Thermally Induced Strain Fields**, ***M.R. Cho***, *P.K. Kim, Y.D. Park*, Seoul National University, Republic of Korea

We demonstrate well-defined path control of nanoscale cracks in SiO_2 thin-films on Si substrate. When cracks are initiated their paths are confined in a predetermined track of arbitrary shape. The confinement of the crack paths is attributed to local thermally induced strain fields. We define the strain fields by utilizing the large differences between coefficients of linear thermal expansion between metallic thin-films and SiO_2. On top of the substrate, a metallic strip of arbitrary shape is first predefined. Next, a layer of SiO_2 is e-beam evaporated, followed by a thermal cycling. We then initiate the cracks by either a predetermined notch or by, more simply, a macro scratch far from the predefined track. Once the leading edge of the crack enters the predefined track, the crack, with width at the surface of SiO_2 of ~50-200 nm, is laterally confined within a width > 2 μm, predefined path length in the millimeter range (or higher), and a minimal turn radius of curvature > 20 μm, and its path shape within the confined track is of nontrivial oscillatory. We present finite element analysis simulations as well as a model that explains and fits well the crack path shape within the track. We also discuss utilizing our results to realize bulk fabrication of nano-gap plasmonic device, nano-gap electrode and nano fluidic channel devices.

9:40am **NS+BI+EM-MoM5 Single-Molecule Surface Enhanced Raman Scattering using Silver Coated Nickel Nanorod Arrays**, ***A. Nash***, *D. Ye*, Virginia Commonwealth University

Nickel nanorods arrays were prepared on silicon (100) substrates using the glancing angle deposition (GLAD) technique. Subsequently, the nanorods were coated with 30 nm thick silver on the tip of the nanorods without breaking vacuum. The surface enhanced Raman scattering (SERS) at near single molecule levels was verified in a Horiba confocal Raman microscope using low concentration Rhodamine 6G. At the concentration 3×10^{-14} M, blinking of the Raman peaks were observed. We found that the Raman signal intensities can be related to the concentration of the analytes by the Langmuir-Freundlich adsorption isotherm.

10:00am **NS+BI+EM-MoM6 Merged Photonic Crystal Slot Waveguide - ALD Coated Silicon Nanophotonics**, ***P. Stenberg***, *M. Roussey, S. Honkanen, M. Kuittinen*, University of Eastern Finland

Research related to Silicon photonics is a topic of high interest in the photonics community. Demands in the field of all optical signal processing are driving research and industry towards faster and more efficient devices and processes. The interest against Silicon is not merely because of the optical characteristics of the material but also because the fabrication of Silicon photonic devices can be adapted to the existing production lines enabling cost efficient mass fabrication.

Our study is focused on a Silicon photonic nanodevice called Merged Photonic Crystal Slot Waveguide (MPCSW), in which features of photonic crystals (PhC) and slot waveguides are compiling, by taking advantage of the slow light effect in the PhC [1] and the field confinement in the slot region [2]. We propose to create the PhC by directly patterning the rails of the slot waveguide. The device is designed on a Silicon on insulator (SOI) substrate and it is coated with amorphous TiO_2 by Atomic Layer Deposition (ALD) technique to fill the structure with optically interesting nonlinear material.

We have studied the possibility to use the device as a band pass filter in near infrared region. The MPCSW structure is designed by using three dimensional Finite Difference Time Domain (3D-FDTD) method to create a photonic band gap (PBG) and a transmission peak appearing in the center of it.

For easier coupling, the input and output waveguides are 3 μm wide and are tapered to nano-waveguides. Coupling from a nano-waveguide to a slot waveguide is made by using an adiabatic coupler to reduce the conversion loss. The adiabatic couplers and nano-to-micro tapers are at both ends of the fabricated waveguide structure. The MPCSW is placed in the middle of the waveguide structure and it contains 10 periods of photonic crystal on both sides of the cavity. The whole device is embedded in conformally coated amorphous TiO_2.

In our presentation we show results concerning simulation and characterization. In simulation we introduce normalized transmission spectra as a function of the fill factor, the cavity length and the period. Also the group index corresponding to the transmission spectra for the same parameters is presented. The fabrication of the structure is discussed where electron beam lithography, plasma etching and ALD techniques are used. Finally we propose possibilities to use the device in nonlinear guided-wave optics by taking advantages of the slow light effect in the PhC and the field confinement in the slot region when the structure is filled with a nonlinear material.

[1] M. Roussey, J. Opt. Soc. Am. B, **24**, 1416-1422, (2007)

[2] A. Säynätjoki, Optics Express, **17**, 21066-21075, (2009)

10:40am **NS+BI+EM-MoM8 Engineering Multimodal Localized Surface Plasmon Resonances in Silicon Nanowires**, *L.-W. Chou,* ***M.A. Filler***, Georgia Institute of Technology

Semiconductors, as a result of their widely tunable carrier density (10^{19} - 10^{21} cm^{-3}), are emerging as promising plasmonic materials for applications in the infrared and near-infrared. Silicon, in particular, is inexpensive relative to the noble metals and benefits from a robust suite of processing tools due to its extensive use in the semiconductor industry. To this end, we recently reported that phosphorus-doped Si nanowires can support mid-infrared localized surface plasmon resonances (LSPRs) with quality factors comparable to those of the noble metals [1]. Herein, we demonstrate that axial control of dopant profile in individual nanowires permits complex, user-programmable, multimodal spectral responses. Highly aligned Si nanowire arrays are synthesized via the vapor-liquid-solid (VLS) technique with a combination of Si- and P-containing precursors. *In-situ* infrared absorption spectroscopy measurements reveal intense absorption bands (5 – 10 um) with dopant concentration and shape-dependent spectral shifts consistent with longitudinal LSPRs. Discrete dipole approximation (DDA) calculations confirm that the observed spectral response results from resonant absorption and free carrier concentrations on the order of 10^{20} cm^{-3}. We also observe near-field coupling between neighboring plasmonic domains, which varies as a function of intrinsic spacer length and can be described with hybridization theory. Our results highlight the utility of VLS synthesis for surface plasmon engineering in semiconductors, create new opportunities to study basic surface plasmon physics, and pave the way for applications including ultra-sensitive molecular detection and thermal energy harvesting.

[1] Chou, L.-W.; Shin, N.; Sivaram, S. V.; Filler, M. A. *J. Am. Chem. Soc.* **2012**, *134*, 16155.

11:00am **NS+BI+EM-MoM9 Exploiting Plasmon Induced Hot Electrons in Molecular Electronic Devices**, *D. Conklin, S. nanayakkara, T.-H. Park,* University of Pennsylvania, *M. Lagadec,* ETH Zürich, Switzerland, *J. Stecher,* Duke University, *X. Chen,* University of Pennsylvania, *M. Therien,* Duke University, ***D.A. Bonnell***, University of Pennsylvania

Plasmonic nanostructures can induce a number of interesting responses in devices. Here we show that hot electrons can be extracted from plasmonic particles and directed into a molecular electronic device, which represents a new mechanism of transfer from light to electronic transport. To isolate this phenomenon from alternative and sometimes simultaneous mechanisms of plasmon-exciton interactions we designed a family of hybrid nanostructure devices consisting of Au nanoparticles and optoelectronically functional porphyin molecules that enable precise control of electronic and optical properties. Temperature and wavelength dependent transport measurements are analyzed in the context of optical absorption spectra of the molecules, the Au particle arrays and the devices. Enhanced photocurrent associated with exciton generation in the molecule is distinguished from enhancements due to plasmon interactions. Mechanisms of plasmon induced current are examined and it is found that hot electron generation can be distinguished from other possibilities.

11:20am **NS+BI+EM-MoM10 Coherent Imaging of Surface Plasmon Dynamics by Time-resolved Photoelectron Emission Microscopy**, ***H. Petek***, University of Pittsburgh **INVITED**

We study surface plasmon polariton (SPP) generation, propagation, diffraction, interference, focusing, and decay by femtosecond time-resolved photoemission electron microscopy (PEEM) and electromagnetic simulations. Equal-pulse pump-probe pulses with interferometrically defined delay excite two-photon photoemission from Ag surfaces. The imaging of the spatial distribution of photoemitted electrons by PEEM reveals a nonlinear map of the total surface electromagnetic fields impressed on the sample. On a nanostructured surface the images reveal coherent polarization gratings consisting of superposition of the incoming excitation pulses and propagating SPP wave packets that are generated at nanofabricated coupling structures. By changing the delay between the pump and probe plusses in steps of ~330 as we record movies of the evolving coherent polarization at the Ag/interface, which reflects the evolution of the surface electromagnetic fields. Through the combination of femtosecond laser excited photoemission and imaging of photoelectrons we can record <10 fs time scale coherent polarization dynamics with ~50 nm spatial resolution. [1]

The SPP fields are generated by specifically designed coupling structures formed by lithographic techniques in Ag films. The physical properties of the coupling structures and the geometry of the excitation define the subsequent SPP dynamics. To obtain a quantitative understanding of the SPP generation and PEEM imaging we perform FDTD calculations on the coupling of the external field into the SPP mode and compare them to experiments for slit coupling structures with different geometries. [4] Using more complicated coupling structures, we demonstrate SPP interference and focusing. [5] Through time-resolved PEEM measurements on nanostructured metal films we will explore the techniques for the coherent control of electromagnetic fields in nanostructured electronic materials on the femtosecond temporal and nanometer spatial scales.

References

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[2] A. Kubo, N. Pontius, and H. Petek, Nano Lett. , 470 (2007).

[3] A. Kubo, Y. S. Jung, H. K. Kim, and H. Petek, J. Phys. B: , S259 (2007).

[4] L. Zhang, A. Kubo, L. Wang, H. Petek, and T. Seideman, Phys. Rev. B , 245442 (2011).

[5] H. Petek and A. Kubo, in *Handbook of Instrumentation and Techniques for Semiconductor Nanostructure Characterization*, Haight, R.; Ross, F.; Hannon, J., Eds. World Scientific Publishing/Imperial College Press: 2011.

Plasma Science and Technology
Room: 102 B - Session PS+AS+BI+SE-MoM

Atmospheric Plasma Processing: Fundamental and Applications

Moderator: M.A. Lieberman, University of California, Berkeley

8:20am **PS+AS+BI+SE-MoM1 Field Emission in Microscale Dimensions: A New Approach to Atmospheric Pressure Gas Discharges**, *Y. Li, P. Rumbach,* ***D.B. Go***, University of Notre Dame **INVITED**

Electron field emission is traditionally considered a low-pressure phenomenon and most field emission-based technologies, such as scanning electron microscopes, generate field emission under high vacuum conditions. However, over the course of past decade, a advances in microscale devices have led to the field emission devices that operate at high pressures, including at and near to atmospheric pressure. At these pressures, the field-emitted electrons can ionize the interstitial gas between the electrodes, leading to the formation of gas discharges. With emerging applications in gas sensing and gas reforming, this new approach to gas discharges not only introduces new, interesting physics but also offers many new technological opportunities. This work will focus on the theory and generation of stable, field emission-driven Townsend discharges. The physical concepts underpinning these discharges will be discussed as theoretical and modeling efforts have highlighted many significant features of this discharge mode – including very high electron densities (~10^{14} cm^{-3}) and highly non-Maxwellian electron densities. Experimental studies and the role of the cathode material will also be discussed as evidence of pressure scaling for field emission will be presented. Finally, new applications and future opportunities for discovery will be covered.

9:00am **PS+AS+BI+SE-MoM3 Simulation of Microplasma Based Pressure Sensors**, ***J-C. Wang***, *Z. Xiong, C. Eun, X. Luo, Y. Gianchandani, M.J. Kushner*, University of Michigan

Pressure monitors in hostile environments often use piezoresistive and capacitive based sensors. The smallest dimension of this class of sensors is about 1 mm. Recently, a microplasma-based pressure sensor has been developed which is capable of dimensions at least an order of magnitude smaller. In these sensors, a plasma is initiated between an anode and two competing cathodes in a sealed chamber having a diaphragm as one surface. External pressure deflects the diaphragm which changes the inter-electrode spacing for one of the anode-cathode pairs, thereby redistributing the current collected by the two competing cathodes. Pressure is then proportional to the relative difference in current collected by the two cathodes.

In this presentation, we will discuss the properties of microplasma-based pressure sensors using results from a two-dimensional simulation. The model, *nonPDPSIM*, solves Poisson's equation, transport equations for charged and neutral species, and the electron energy conservation equation for electron temperature. Radiation transport is addressed using a Green's function approach, and sheath accelerated electrons are addressed using Monte Carlo methods. The microplasma is sustained between an anode (A) biased with hundreds of volts and two grounded cathodes (K_1, K_2) in a sealed chamber filled with 1 atm of Ar or rare gas mixtures. The reference cathode (K_1) is located adjacent to the anode while the sensing cathode (K_2) is mounted on the diaphragm separated by a gap of 10 to 100 μm. We find that following a small amount of electric field emission of electrons from the edges of K_1 and K_2, the electrons rapidly avalanche in the geometrically enhanced electric field at the edge of the anode and creates a conductive plasma within tens of ns. The current distribution on K_1 and K_2 varies with inter-electrode spacing (AK_2) which is changed by deflection of the diaphragm due to the external pressure. The current distribution can also be optimized by adjusting the impedance connected to electrodes.

*Work was supported by the Advanced Energy Consortium.

9:20am **PS+AS+BI+SE-MoM4 A Flexible Paper-based Microdischarge Array Device for Maskless Patterning on Nonflat Surfaces**, ***Y.J. Yang****, *M.Y. Tsai, W.C. Liang, H.Y. Chen, C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

This study presents a simple and economical paper-based microdischarge array for maskless surface patterning under atmospheric pressure condition. This paper-based system is a dielectric-barrier-discharge (DBD)-type device and stable plasmas can be sustained in an array of cavities. Due to its flexible feature, this paper-based device allows for performing non-flat surface patterning processes with a feature size down to 500 μm. When a flat or a curved glass surface with 6 mm in its curvature is directly treated by the Ar plasma generated by this device, hydrophilic spots can be generated on the flat or curved surface, respectively. While using tetraglyme as the precursor in Ar atmosphere, this paper-based device is able to perform plasma polymerization and to pattern polyethylene oxide (PEO)-like array of patterns on glass surfaces. Under this arrangement, the optical emission spectrum emanating from the plasma show CO emissions at 561 nm during the deposition process, suggesting that the participation of precursor molecules in the process. The FTIR spectra of deposited films show absorption of C-O-C bonding at 1100 cm^{-1}, indicating retaining of ether groups. To test the anti-fouling property of this film, Alexa Fluor 546-conjugated fibrinogen was utilized as a model reporter molecule for protein absorption test. The fluorescence image shows clear contrast between the coated and non-coated area. The PEO-pattered regions appear to be dark since no protein absorption occurs. This work demonstrates a flexible and cost-effective approach to pattern flat and non-flat surfaces with a maskless process. This work was supported by National Science Council of Taiwan, the Republic of China (101-2221-E-002-163-MY2)

9:40am **PS+AS+BI+SE-MoM5 Hydrophobic Fluorocarbon Films Synthesized from Liquid Monomers by Atmospheric Pressure Plasma**, ***J. Hubert***, *N. Vandencasteele, T. Dufour,* Univ. Libre de Bruxelles, Belgium, *C. Poleunis,* Univ. catholique de Louvain, Belgium, *P. Laha,* Vrije Univ. Brussel, Belgium, *P. Viville,* Materia Nova, Belgium, *A. Delcorte, P. Bertrand,* Univ. catholique de Louvain, Belgium, *H.A. Terryn,* Vrije Univ. Brussel, Belgium, *R. Lazzaroni,* Materia Nova, Belgium, *F.A.B. Reniers*, Univ. Libre de Bruxelles, Belgium

The exceptionally low surface energy of polytetrafluoroethylene (PTFE), due to the CF_2 functional groups present on its surface gives the polymer advantageous properties such as hydrophobicity. In order to create PTFE-like films, low pressure plasma deposition of fluorocarbon films has been extensively studied in the last decade. These works focus however on the use of gaseous precursors such as CF_4, C_2F_6 or C_4F_8.

In the present study, hydrophobic fluorocarbon coatings have been synthesized from two different precursors, which are liquid at room temperature. Perfluorohexane (C_6F_{14}), a fully saturated monomer and perfluoro(2-methylpent-2-ene) (C_6F_{12}) containing one unsaturated bond are injected in a dielectric barrier discharge (DBD) by a continuous argon or helium flow. In order to characterize the plasma polymer films and the texturization process, both, analysis of the surface and the gas phase have been performed.

Secondary ion mass spectrometry (SIMS) and X-ray photoelectron spectroscopy (XPS) measurements have been performed to highlight the structure and composition of the C_xF_y films depending on the Yasuda factor (W/FM), throughout the influence of the power and the monomer flow rate. Water contact angle (WCA) measurements have shown that the hydrophobicity properties of the fluorocarbon films were similar to that of PTFE as WCA of 110° have been obtained. However, the structure also depends on the nature of the carrier gas (argon or helium) and in some cases, WCA as high as 140° were achieved. Atomic force microscopy AFM measurements are used to correlate the increase in hydrophobicity with the increase in roughness, which could be linked to the film thickness.

In order to complete the analysis of the polymerization process, mass spectrometry (MS) and optical emission spectroscopy (OES) have been performed. Fluorocarbon compounds such as CF, CF_2, CF_3, or higher mass fragments such as C_3F_3 or C_2F_4 have clearly been identified. Their detection combined to the SIMS analysis could help us to understand the polymerization mechanism/reaction of the two precursors.

10:00am **PS+AS+BI+SE-MoM6 Deciphering Gas-Phase and Solution-Phase Reactions Initiated by Plasmas at the Surface of Aqueous Solutions**, ***P. Rumbach***, University of Notre Dame, *R.M. Sankaran,* Case Western Reserve University, *D.B. Go*, University of Notre Dame

Recent advancements in atmospheric-pressure plasma technology have enabled applications in polymer processing, plasma medicine, and water treatment. Many of these applications rely heavily on physical and chemical interactions between plasmas and aqueous solutions. We have recently shown that plasma electrons are involved in electrolytic reactions such as the reduction of aqueous hydrogen ions (H+) to hydrogen gas[1]. In this work, we show that the reactions are more complex and involve a competition between plasma chemistry and solution chemistry.

To study interactions between a plasma and liquid, saline solutions were exposed to an argon (Ar) DC microplasma jet, and the effects of various reactions occurring in the plasma and solution phase were characterized. When the plasma jet was run in a background of argon or oxygen gas, traditional electrolytic reactions yielding sodium hydroxide (NaOH) were found to be dominant, making the solution more basic (pH ~ 8). Running

*** Coburn & Winters Student Award Finalist**

the plasma jet in a background of atmospheric air produced significant amounts of nitric acid (HNO_3) and hydrogen peroxide (H_2O_2) in solution. Production of HNO_3 in air typically occurs at a rate two orders of magnitude higher than NaOH, making the solution more acidic (pH ~ 3). In a background of nitrogen gas, HNO_3 was also produced, but at a rate that is limited by oxygen gas evolution from water electrolysis. Overall, the chemical composition of the solution is affected by both electrolytic reactions at the plasma-liquid interface as well as reactions occurring in the bulk plasma.

[1] M. Witzke, P. Rumbach, D. B. Go, and R. M. Sankaran, *J. Phys. D: Appl. Phys*. **45**, 442001 (2012).

10:40am **PS+AS+BI+SE-MoM8 Prostate Cancer Treatment using Low-Temperature Atmospheric Pressure Plasmas: Advanced Optical Diagnostics and Multi-scale Numerical Simulations**, ***D. O'Connell***, University of York, UK **INVITED**

Non-equilibrium plasmas, operated at ambient atmospheric pressure and temperature, are very efficient sources for highly reactive neutral particles e.g. reactive oxygen and nitrogen species (RONS) (such as atomic oxygen, atomic nitrogen, nitrogen oxides), charged particles, UV-radiation, and electro-magnetic fields. Individually many of these components have been implicated in therapeutics. Plasmas have the advantage of delivering these components simultaneously providing potentially superior processes through synergies. This has led to the establishment of low-temperature plasmas with potential in disease therapeutics and plasma pharmacology. The challenges lie in understanding the mechanism of interaction, quantifying and accurately tailoring the plasma and its power dissipation. Suitable optimized plasma sources are currently lacking, and improbable through empirical investigations. Therefore, quantifying the power dissipation and energy transport mechanisms through the different interfaces from the plasma regime to ambient air, towards the liquid interface and associated impact on the biological system through a new regime of liquid chemistry initiated by the synergy of delivering multiple energy carrying species, is crucial.

This presentation will include examining our interaction studies of atmospheric pressure plasma jets with prostate cancer cells and our results of employing advanced diagnostic techniques for direct measurements of reactive plasma species and comparison to chemical kinetics simulations. These include absolute densities of atomic oxygen and atomic nitrogen using non-linear laser spectroscopy and vacuum ultra-violet (VUV) absorption spectroscopy, where the VUV radiation was produced using a synchrotron and detected with a high-resolution Fourier-transform spectrometer.

11:20am **PS+AS+BI+SE-MoM10 Conformal Encapsulation of Three-Demensional, Bioresorbable Polymeric Scaffolds Using Plasma Enhanced Chemical Vapor Deposition**, ***M. Hawker***, *A. Pegalajar-Jurado, E.R. Fisher*, Colorado State University

Bioresorbable polymers such as poly(ε-caprolactone) (PCL) have a multitude of potential biomaterial applications such as controlled-release drug delivery and regenerative tissue engineering. Fabricating these polymers into porous, three-dimensional (3D) materials is critical for such biological applications to maximize their surface-to-volume ratio, mimic the extracellular matrix, and increase drug-loading capacity. Three-dimensional porous PCL scaffold materials have been fabricated via the porogen leaching method. These scaffolds can be plasma-treated to improve or modify their surface properties while maintaining the desirable bulk polymer characteristics. For example, plasma polymerization can be used to encapsulate the polymer scaffold, thereby potentially providing a mechanism for controlled release drug delivery. Here, two different fluorocarbon (FC) precursors, octofluoropropane (C_3F_8) and hexafluoropropylene oxide (HFPO), were used to deposit FC films on PCL scaffolds using plasma enhanced chemical vapor deposition. X-ray photoelectron spectroscopy (XPS) analysis showed that high-CF_2 content films were deposited on the PCL scaffolds, similar to those previously deposited in our labs on one-dimensional and two-dimensional materials. Cross-sectional XPS data demonstrated that FC film deposition occurred both on the outer scaffold surface and throughout the 3D structure. Scanning electron microscopy data confirmed that FC film deposition yielded conformal rather than blanket coatings as the porous scaffold structure was maintained after plasma treatment. Additional parameter studies suggest that treatment time, substrate location, and precursor gas have significant impact on the nature of the deposited films. This work demonstrates that conformal FC coatings can be deposited on 3D polymeric scaffolds using plasma processing. Results from cell adhesion studies as well as other film deposition systems and alternate bioresorbable scaffold materials will also be presented.

11:40am **PS+AS+BI+SE-MoM11 Deactivation of Lipopolysaccharide by an Atmospheric Pressure Plasma Jet**, ***E.J. Bartis***, *C. Hart, Q. Yang*, University of Maryland, College Park, *T.-Y. Chung, D.B. Graves*, University of California, Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland, College Park

Low temperature plasma treatment of surfaces has been shown to degrade and sterilize bacteria as well as deactivate harmful biomolecules. However, a major knowledge gap exists regarding which plasma species are responsible for the modifications required for deactivation. Lipopolysaccharide (LPS) and lipid A, the toxic element of LPS, are the main components of the outer membrane of Gram-negative bacteria and induce a strong immune response in animals. In this study, LPS-coated silicon substrates were exposed to the effluent of an atmospheric pressure plasma jet (APPJ) under a controlled environment to examine the effect of plasma-generated reactive species on the surface chemistry and biological activity. Additionally, spatially-resolved optical emission spectroscopy, UV absorption spectroscopy, and electrical characterization were performed on the jet to identify and characterize plasma-generated species. Biological activity of LPS was measured using an enzyme-linked immunosorbent assay (ELISA) and correlated with changes in surface chemistry measured by vacuum transfer to x-ray photoelectron spectroscopy (XPS). The kHz-driven atmospheric pressure plasma jet consists of two tubular electrodes surrounding an alumina tube. By flowing Ar with small admixtures of O_2/N_2 through the tube and applying a high voltage across the electrodes, the plasma ignites to form a stable jet. The species that arrive at the sample can be regulated by adjusting the distance from the source to the sample. At longer source-to-sample distances, species with short lifetimes will not reach the sample. Adding oxygen to the gas flow causes the most significant changes. For source-to-sample distances > 10 cm, where radical species dominate, higher levels of deactivation were observed for O2/Ar plasma than for Ar and N_2/Ar plasmas. O_2/N_2/Ar plasma showed decreased deactivation compared to O_2/Ar plasma with the same O_2 admixture due to creation of NO_x, whose formation consumes reactive oxygen species. With XPS, we observed that O_2-containing discharges remove C-C bonding from the surface while N_2-containing discharges cause minimal changes. XPS studies of APPJ-treated films showed that deactivation depends on C-C bonding measured in the C 1s, which depends on the admixture of O_2 into the APPJ. The decrease in C-C bonding correlates with the loss of lipid A's aliphatic chains, which are partially responsible for its toxicity. The authors gratefully acknowledge financial support from US Department of Energy (DE-SC0005105 and DE-SC0001939) and National Science Foundation (PHY-1004256).

Biomaterial Interfaces
Room: 201 B - Session BI+AI+BA+IS-MoA

Biofouling
Moderator: D.E. Barlow, Naval Research Laboratory

2:00pm **BI+AI+BA+IS-MoA1 Biofouling of Carbon Steel: Effects of Microstructure and Test Media on Initial Bacterial Attachment and Subsequent Corrosion**, *M.A. Javed, P.R. Stoddart, S.M. McArthur,* ***S.A. Wade***, Swinburne University of Technology, Australia

Biofouling of surfaces causes numerous problems in a wide range of industries such as shipping, health care, oil and gas production and food production. Of specific interest to the current work is the accelerated corrosion of metals that can arise as a consequence of bacterial biofilm formation, which is commonly known as microbiologically influenced corrosion (MIC).

The initial attachment of bacteria to a surface is one of the first steps in the process of biofouling. The attachment is dependent upon a large number of factors, which are broadly related to the properties of the bacteria, substrate/surface and environment. Changes in these properties can not only influence the initial attachment step, but also the interrelated production of extracellular polymeric substances (EPS) by the bacteria and the subsequent corrosion.

A large amount of the work performed to date on bacterial attachment in relation to MIC has focused on stainless steels, possibly due to reports of rapid failures of these materials such as through thickness pitting of piping welds. These studies have highlighted how a range of material properties (e.g. chemical composition, surface roughness, grain size and boundaries) can influence attachment and biofilm formation on steel surfaces. This range of influences means that a high level of care must be taken when designing and carrying out bacterial attachment tests in order to avoid the situation where a number of material variables affect the outcome of a single test. For example one of the criticisms of some of the previous work in this area is the lack of control of surface roughness of the substrates used in the studies.

In this work we will report results of studies of the initial attachment and EPS production of *E. coli* bacteria on highly polished carbon steel samples, with a number of different microstructures, for a number of different test media. We have found that the microstructure and test medium can have a significant effect on the rate of bacterial attachment, the distribution of attached bacteria, the onset of EPS production and the corrosion of samples immersed in *E. coli* inoculated test media.

2:20pm **BI+AI+BA+IS-MoA2 Charged SAMs as Model Surfaces to Understand Anti-fouling Properties of Zwitterionic Coatings**, ***S. Bauer***, University of Heidelberg, Germany, *J. Finlay, M.E. Callow, J.A. Callow,* University of Birmingham, UK, *A. Rosenhahn*, Ruhr-University Bochum, Germany

Zwitterionic surfaces are a class of coatings that receive increasing attention due to their good antifouling performance.[1] Since early work on protein resistance of mixed, charged self-assembled monolayers (SAMs), charge neutrality seems to be a prerequisite for their inert properties. [2,3] Similar to established non-fouling ethylene glycol chemistries, zwitterionic systems rely on a strong hydration of the coating. In this study we attempt a systematic analysis to which extend charge neutrality and the chemical nature of the charged groups affect their antifouling performance. Positively charged trimethylammonium terminated thiols were therefore mixed with sulfonate-, carboxylate- and phosphonate-terminated undecanethiols in varying ratios. Optimized preparation conditions and surface analysis will be presented that demonstrates successful assembly of the coatings and characterizes their physicochemical properties. The antifouling properties were tested against a range of laboratory organisms such as diatoms and spores of algae and compared to protein resistance. The obtained trends will be discussed and correlated with field experiments in the real marine environment.

(1) Chen, S.; Jiang, S. **2008** A new avenue to nonfouling materials. *Advanced Materials*, 20, 335-338.

(2) Holmlin, R. E.; Chen, X. X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M. **2001** Zwitterionic SAMs that resist nonspecific adsorption of protein from aqueous buffer. *Langmuir*, 17, 2841-2850.

(3) Chen, S. F.; Yu, F. C.; Yu, Q. M.; He, Y.; Jiang, S. Y. **2006** Strong resistance of a thin crystalline layer of balanced charged groups to protein adsorption. *Langmuir*, 22, 8186-8191.

2:40pm **BI+AI+BA+IS-MoA3 The Role of Bacterial Physiology in Biodeterioration of Polyurethane Coatings**, *S. Zingarelli,* Air Force Research Laboratory, *D.E. Barlow, J.C. Biffinger,* Naval Research Laboratory, *L.J. Nadeau,* Air Force Research Laboratory, *D. Babson,* Naval Research Laboratory, *B.W. Stamps,* University of Oklahoma, *R.K. Pirlo,* Naval Research Laboratory, *C.N. Drake,* Air Force Research Laboratory, *B.S. Stevenson,* University of Oklahoma, *J.N. Russell, Jr.,* Naval Research Laboratory, ***W.J. Crookes-Goodson***, Air Force Research Laboratory **INVITED**

Microbial biofilms frequently contaminate surfaces and can cause degradation of polyurethane coatings that are intended to protect against environmental degradation. Historically, investigations of polyurethane biodeterioration have focused on identification and characterization of the organisms and 'polyurethanase' enzymes involved in the degradation process. However, many questions remain unanswered. For example, microbes capable of polymer degradation are ubiquitous in the environment, yet only affect polymers under some circumstances. What controls the production of polyurethanases? What is the role of planktonic vs. biofilm populations in the biodeterioration process? The goal of our research is to define the parameters and regulatory mechanisms that result in polyurethane biodeterioration by *Pseudomonas protegens Pf*-5, with a focus on environmental conditions (nutrients, pH, oxygen) and microbial 'lifestyles' (planktonic vs. biofilm populations). First, we screened a variety of carbon sources with a polyurethane agar plate-clearing assay using the polyester polyurethane Impranil DLN. Results showed that strain *Pf*-5 could grow on a variety of carbon sources but that degradation of polyurethane varied depending on the carbon source. We observed strong polyurethane degradation in the presence of M9-citrate medium but severely reduced clearing of polyurethane when glucose was provided as a carbon source. Subsequent studies with planktonic cultures of *P. protegens Pf*-5 verified the inhibitory effect of glucose on polyurethanase activity. Using proteomic tools, activity in citrate-grown planktonic culture supernatants was ascribed to two esterases, polyurethane esterases A and B. Currently the regulation of these enzymes is being investigated through a combination of genetic and transcriptomic approaches. Biofilms were grown on Impranil DLN in M9-citrate or -glucose to determine if these nutrients also regulated polyurethanase secretion in biofilms. Micro ATR-FTIR surface chemical analysis of the coatings after biofilm removal showed that degradation proceeds through preferential loss of the ester component. However, optical microscopy and profilometry clearly show that subsequent bulk coating loss can occur under certain conditions, resulting in complete loss of the original coating surface, and eventually complete loss of the coating. Transmission FTIR microscopy was also used to detect bulk coating degradation in a biofilm culture plate assay we developed to complement the Impranil clearing assay. This assay demonstrated significant Impranil coating degradation from citrate-grown biofilms versus minor degradation for glucose-grown biofilms.

3:40pm **BI+AI+BA+IS-MoA6 Multifunctional Active Nano and Microstructured Surfaces for Biofouling Management**, ***G.P. López***, Duke University **INVITED**

This talk will present (i) recent developments of stimuli responsive surfaces that exhibit dynamic structure on lateral length scales of the order of 10 microns and below, (ii) a prospectus for the formation of multifunctional bioactive surfaces based on such dynamic micro- and nanostructured materials, and (iii) results from study of bioadhesion and biorecognition on these surfaces. Stimuli responsive polymer surfaces include patterned polymer brushes and elastomers; biological systems of interest include protein solutions, adherent mammalian cell lines, as well as marine and infectious bacteria. Our previous studies have demonstrated that stimuli responsive polymers can be used to control the adhesion of such systems and, in this presentation, we will provide our latest advancements in this line of study, as regards to both molecular and cellular biointerfacial phenomena. Methods for preparing dynamic micro- and nanopatterns of stimuli responsive polymers will be presented, along with characterization of their structure, dynamic behavior and bioadhesion resistant character.

4:40pm **BI+AI+BA+IS-MoA9 Roles of Extracellular DNA in the Development and Expansion of Bacterial Biofilms**, ***C.B. Whitchurch***, University of Technology, Sydney, Australia **INVITED**

Biofilms are multicellular communities of bacteria that are often found attached to surfaces and cause significant problems in medical, industrial, and marine settings. Cells within biofilms are enmeshed in an extracellular polymeric matrix comprised of polysaccharides, proteins, lipids, and nucleic acids. Over the past decade, extracellular DNA (eDNA) has been found to be essential for biofilm formation by many species of bacteriawhere it is

thought to function as an intercellular "glue" that binds cells together. Interestingly, whilst it has been known for over a decade that eDNA is essential during the early stages of biofilm development by the opportunistic pathogen *Pseudomonas aeruginosa*, the precise roles of eDNA in this process have yet to be elucidated. We have used advanced techniques in microscopy, computer vision and image informatics to explore the roles of eDNA during early biofilm development and during active expansion of biofilms formed by *P.aeruginosa*. Many species of bacteria, including *P. aeruginosa* utilize type IV pili mediated twitching motility to actively translocate across solid and semi-solid surfaces. Twitching motility can manifest as a complex, multicellular behavior that enables the active expansion of bacterial biofilms. Under appropriate conditions, such as those encountered at the interface of a glass coverslip and semi-solid nutrient media, the expanding biofilm can develop dramatic networks of intersecting trails. Our analyses reveal that at the leading edge of the interstitial biofilm, highly coherent groups of bacteria migrate across the surface of the semi-solid media, and in doing so, create furrows along which following cells preferentially migrate. This leads to the emergence of a network of trails that guide mass transit toward the leading edges of the biofilm. We have determined that eDNA facilitates efficient traffic flow throughout the expanding biofilm by maintaining coherent cell alignments, thereby avoiding traffic jams and ensuring an efficient supply of cells to the migrating front. Our analyses reveal that eDNA also co-ordinates the movements of cells in the leading edge rafts and is required for the assembly of cells into aggregates that forge the interconnecting furrows. Our observations have revealed that large-scale self-organization of cells in actively expanding biofilms of *P. aeruginosa* occurs through construction of an intricate network of furrows that is facilitated by eDNA.

5:20pm **BI+AI+BA+IS-MoA11 Sample Preparation and Optimization for Bacterial Identification by Raman Spectroscopy**, ***M.M. Hlaing***, *M. Dunn, S.M. McArthur, P.R. Stoddart*, Swinburne University of Technology, Australia

The characterisation and identification of individual bacteria using Raman spectroscopy can aid in rapid, in situ microbiological diagnosis and hence timely, appropriate treatment and control measures [1, 2]. Appropriate sample preparation methods and experimental conditions are crucial to avoid some potential difficulties in analysing the information-rich Raman spectra from bacterial cells. In this study, the Raman spectra of fresh and stored samples of bacterial isolates (*Escherichia coli*) were analysed to determine any variations caused by sample processing. Analysis based on principal components suggests that different methods of sample preparation and storage affect the spectral components associated with different biochemical compounds in bacterial cells. The effect of long term storage in glycerol stock at freezing temperatures on the Raman spectrum of cells from the early exponential phase was observed in this study and found to modify the bacteria cells. Furthermore, the presence of extracellular polymeric substance (EPS) matrix around bacterial cells at later stages of the growth cycle provide higher resistance to environmental stress compared with other phases. Based on these results, a specific experimental protocol has been developed in order to obtain interpretable, comparable and reliable Raman data from bacterial samples.

Keywords: Raman spectroscopy; Bacterial identification; Sample preparation.

References

[1] W. E. Huang, R. I. Griffiths. Anal. Chem. 2004, **76**(15): 4452-4458.

[2] T. J. Moritz, S. T. Douglas. J. Clin. Microbiol. 2010, **48**(11): 4287-4290.

Ions at Aqueous Interfaces Focus Topic
Room: 203 A - Session IA+AI+BI+IS+NL+SS-MoA

Ions at Aqueous Interfaces
Moderator: M.H. Grunze, University of Heidelberg, Germany

2:00pm **IA+AI+BI+IS+NL+SS-MoA1 Sum-frequency Vibrational Spectroscopy for Studies of Ions Emerging at Water Interfaces**, ***Y.R. Shen***, University of California, Berkeley **INVITED**

Ions at water interfaces can significantly change the chemical and physical properties, and hence the functionality, of the interfaces. They play a key role in many important processes in many disciplines. In recent years, sum-frequency vibrational spectroscopy(SFVS) has been demonstrated to be a unique, effective tool to study such interfaces. We discuss here SFVS investigations of ions at various water interfaces: soluble ions at air/water interfaces, ions attached to Langmuir monolayers on water, and hydrophilic and hydrophobic water interfaces. Formation of an electric double charge layer by ions near an interface usually occurs. It induces significant polar reorientation of interfacial water molecules and alters their vibrational spectra that can be detected by SFVS. Useful structural information can be deduced from the results, but work is still needed for complete understanding of the results.

2:40pm **IA+AI+BI+IS+NL+SS-MoA3 Experimental Quantification of Surface Propensity of Halide Ions by Femtosecond Surface Vibrational Spectroscopy**, ***M. Bonn***, Max Planck Institute for Polymer Research, Germany, *H.J. Bakker*, FOM Institute AMOLF, Netherlands, *Z. Zhang, E.H.G. Backus*, Max Planck Institute for Polymer Research, Germany, *L. Piatkowski*, FOM Institute AMOLF, Netherlands **INVITED**

We investigate the vibrational dynamics and energy transfer between interfacial water molecules, in the presence of sodium chloride and sodium iodide salts, using 2-dimensional, femtosecond surface-specific vibrational spectroscopy. We find that both the vibrational lifetime and the intramolecular energy transfer for anion associated interfacial water molecules is slower than for non ion-bound interfacial water molecules. The analysis of the time-dependent slope of the 2-dimensional sum frequency response reveals that the intermolecular resonant energy transfer between the interfacial water molecules is significantly slowed down by the presence of ions. Accordingly, the decay of the frequency-frequency correlation function is slower for NaI than for NaCl solution. This finding provides direct evidence of the higher surface propensity for iodide than for chloride ion, and allows for the quantification of interfacial density of halide ions for both systems.

3:40pm **IA+AI+BI+IS+NL+SS-MoA6 Specific Ion Effects on Acid-Base Equilibria at the Planar Silica/Water Interface**, ***J.M. Gibbs-Davis***, University of Alberta, Canada

The interaction of ions with biological and environmental interfaces depends not only on their valency but also their identity. These specific ion interactions can influence other processes like deprotonation at mineral oxide interfaces. To monitor such interactions we utilized surface specific second harmonic generation (SHG) to report on changes in the surface charge density of silica in real time. We observe that the intrinsic equilibrium constant of the silanol groups is sensitive to the identity of the alkali ion. In contrast, varying the identity of the anion does not affect the intrinsic acidity of the sites but rather their mechanism of deprotonation. Specifically, positive cooperativity is observed in the deprotonation of silanol groups with increasing anion size and polarizability. These results and complementary measurements of the water structure using sum frequency generation spectroscopy will be discussed.

4:00pm **IA+AI+BI+IS+NL+SS-MoA7 Molecular Insight Into the Preferential Adsorption of Monovalent Ions to Selected Polar Surfaces: A Vibrational Sum Frequency Study**, ***E.C. Tyrode***, *R. Corkery*, KTH Royal Institute of Technology, Sweden

Vibrational Sum Frequency Spectroscopy (VSFS) has been used to systematically study the preferential adsorption of a series of monovalent ions to charged and uncharged fatty acid monolayers. Ion enrichment is mainly determined indirectly by targeting surface water vibrational modes. In selected cases however, the ion presence is also directly determined by targeting the fatty acid carboxylate headgroups. A major effort is made to understand the effect of co-ions in the molecular properties of these biophysically relevant interfaces.

4:20pm **IA+AI+BI+IS+NL+SS-MoA8 Dielectric Interfacial Effects**, ***R. Netz***, FU Berlin, Germany **INVITED**

The molecular layer of water molecules on surfaces, the so-called hydration layer, is important for a whole number of properties of biological as well as technological surfaces. Insight can be gained from all-atomistic simulations in conjunction with appropriate continuum modeling.

- Dielectric properties of interfacial water layers are important for the design of high-power capacitors, and can be resolved using simulations.

- At the same time, ions accumulate into a highly condensed interfacial layer, leading to the well-known saturation of the electro-osmotic mobility at large surface charge density regardless of the hydrodynamic boundary conditions. The experimentally well-established apparent excess surface conductivity follows for all hydrodynamic boundary conditions without additional assumptions.

- Hydration water at biological membranes absorbs electromagnetic radiation specifically in the 0.1-10 GHz range that is used for radio communication. Possible health issues are discussed.

5:00pm **IA+AI+BI+IS+NL+SS-MoA10 Liquid Jet –XPS Studies of Ions and Nitriles at the Aqueous Interface**, ***K.A. Perrine***, *M.H.C. Van Spyk, A.M. Margarella,* University of California, Irvine, *H. Bluhm,* Lawrence Berkeley National Laboratory, *B. Winter,* Helmholtz-Zentrum Berlin für Materialien und Energie/Elektronenspeicherring BESSY II, Germany, *M. Faubel,* Max Planck Institute for Dynamik und Selbstorganisation, Germany, *J.C. Hemminger*, University of California, Irvine

Acetonitrile in water is known to exhibit non-ideal behavior. At low concentrations, acetonitrile molecules migrate towards the solution interface leaving water mostly in the bulk. At 0.2 mole fraction, the surface saturates with a full monolayer. Above 0.2 mf, the acetonitrile signal at the surface is enhanced relative to that of the bulk with increasing solution concentration. In the bulk, acetonitrile and water form clusters between 0.2 and 0.7 mole fraction and interact with each other through dipole interactions. Propionitrile, another nitrile with a lower solubility, is also shown have a propensity for the surface of aqueous solutions.

Ions have been shown to impact the properties and solvation structure of aqueous solutions, both at the surface and in the bulk of solution. Potassium iodide (KI) was added to acetonitrile and propionitrile aqueous solutions to observe the effects of ions on nitrile distributions. Liquid jet-X-ray photoelectron spectroscopy (LJ-XPS) was used to characterize the elemental compositions of ions and nitrile species. By tuning the incident photon energy, different depths of the solutions is observed; at low kinetic energies the solution surface is probed and the high kinetic energies the bulk of solution is probed. After adding KI, the interfacial photoelectron spectroscopy signal reveals a reduction in nitrogen and carbon signals in acetonitrile, demonstrating the salting-in effect. With addition of ions to aqueous propionitrile solutions, nitrogen and carbon signals are increased, suggesting a salting-out effect. Sodium chloride ions are also added to aqueous propionitrile studies to determine differences between ions effects from the KI and NaCl salts on propionitrile solutions. These studies help elucidate the role ions play at the interface of aqueous organic solutions.

5:20pm **IA+AI+BI+IS+NL+SS-MoA11 Study of the Structural and Adhesion Forces in Highly Concentrated Electrolytes using Atomic Force Microscopy (AFM)**, ***T. Baimpos***, *M. Valtiner*, Max Planck Institut fur Eisenforschung GmbH, Germany

The understanding of the surface interaction in electrolyte solutions is of paramount importance in many fields such us biology, electrochemistry and surface chemistry. Aqueous solutions of high concentrations are mainly interesting from practical point of view (batteries). In principle, AFM through the Force versus Distance curves (F-D) can be successfully used to probe the electrolyte layering at solid-liquid interfaces and investigate the nature of hydration forces in the presence of various electrolytes of different ion valency, ion concentration or pH [1].

In the current work AFM has been used to measure hydration forces between a non-coated Silicon colloid probe and atomically smooth, flat freshly cleaved Mica surfaces, in highly concentrated monovalent electrolytes (LiCl, NaCl, CsCl). The effect of i) the cation hydration diameter ($Li^+ > Na^+ > Cs^+$) and ii) the electrolyte's concentration (0.05-3.0 M), on both the structural (F_{STR}) and adhesion (F_{ADH}) forces are studied. In all environments, F_{ADH} values pass through a minimum as a function of electrolyte's concentration, while for each salt solution, the frequency of structural events is calculated as a function of its concentration. The number of the F-D curves, were classified in appropriate tables according to the number of the structural hydration layers observed. Furthermore, depending on the concentration, 1, 2 or even up to 5 consecutive hydration layers can be clearly distinguished in the same F-D curve from which both the force and the range of each layer can be measured. These results are compared with the hydrated radii of the above ions enabling the extrusion of useful statements concerning the re-arrangement of the structured cation/water layer at the liquid/solid interface.

Biomaterial Interfaces
Room: 201 B - Session BI+AS+BA+NL-TuM

Biointerface, Energy and Environmental Applications of QCM

Moderator: L. Hanley, University of Illinois at Chicago

8:00am **BI+AS+BA+NL-TuM1 QCM-D for Energy and Environmental Applications**, ***B.H. Kasemo***, Chalmers University of Technology, Sweden **INVITED**

QCM-D has over the past ca. 15 years matured to a measurement technique with a manifold of applications for liquid or gas phase applications. "D" stands for *dissipation* or damping of the sensor oscillation. It yields new information about sample visco-elastic properties, in addition to the mass changes at the ng/cm^2 level obtained from the QCM frequency shift. New information is obtained when the overlayer or film that is studied, causes significant energy dissipation. This is e.g. the case with viscous or visco-elastic films and molecular adlayers. In such cases the two independent quantities, the frequency shift Δf and the dissipation change ΔD , via modeling, allow unique new information to be extracted from the measurements, compared to conventional QCM. In addition, the magnitude of ΔD provides an immediate hint if the Sauerbrey relation, converting Δf to a proportional change in mass, is applicable or not. Major application areas of QCM-D in the past and currently are biomolecule adsorption on surfaces, e.g. on medical implant materials, supported lipid bilayers mimicking cell membranes, polyelectrolytes e.g. layer-by-layer growth, polymer coatings and their curing and phase changes, and more recently cell and bacterial studies. Well over 1200 QCM-D publications have been produced in these areas, cited over 15 000 times. More recently studies related to applications in the energy and environmental areas have rapidly increased. Energy technology examples include solar cells (dye impregnation of DSSC), fuel cell electrode corrosion, studies related to fossil fuel properties and processes, hydrogen storage and CO2 capture/sorption. In the environmental area many applications relate to nanoparticle safety and toxicity, e.g. measuring (surface) affinities between NPs and other materials or agglomeration between NPs. Yet another growing area is to use supported lipid membranes as up-stream model and screening systems, mimicking cell membranes, for testing of NP affinity to such membranes. The method is also used for other aspects of waste water cleaning, such as measuring affinities to filtering materials and membranes of heavy metal ions and other impurities.

9:00am **BI+AS+BA+NL-TuM4 Accounting for Unintended Binding Events in the Analysis of Quartz Crystal Microbalance Kinetic Data**, ***G. Heller***, *T. Zwang, M. Sazinsky, A. Radunskaya, M.S. Johal*, Pomona College

Previous methods for analyzing protein-ligand binding events using the Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) fail to account for unintended binding that inevitably occurs during surface measurements and obscure kinetic information. In this talk, I present a system of differential equations that accounts for both reversible and irreversible unintended interactions. This model is tested on three well-characterized protein-ligand systems, each of which has different features, to establish the feasibility of using the QCM-D for protein binding analysis. The first system presented is the binding of hemin to human serum albumin. The second is the binding of Fe (III) 2,5-dihydroxybenzoic acid complex to neutrophil gelatinase-associated lipocalin tagged with glutathione S-transferase. The third system presented is the interaction of caffeine and bovine serum albumin. Characteristics of the QCM-D binding data for these three systems that are inconsistent with previous QCM-D kinetic models are 1) a non-constant deposition rate in the association phase, 2) a non-zero mass near the steady state of the rinse phase, 3) a non-linear dependence on ligand concentration, and 4) a non-constant ligand concentration for runs lasting short periods of time. Our model accounts for these factors and demonstrates the feasibility of using QCM-D to extract kinetic information and accurately determine affinity constants (K_d) for protein-ligand complexes.

9:20am **BI+AS+BA+NL-TuM5 Silica Nanoparticle – Lipid Membrane Interaction Studies Towards Nano(Q)SAR?**, *L. De Battice, R. Frost,* Chalmers University of Technology, Sweden, *A. Sundblom, M. Persson,* AkzoNobel PPC, Sweden, *M. Wallin, J. Sturve,* University of Gothenburg, Sweden, ***S. Svedhem***, Chalmers University of Technology, Sweden

To improve on the performance of silica-based nanomaterials, and to reduce environmental and health risks related to this development, it is important to learn about how engineered nanomaterials interact with e.g. biomolecules and biological barriers. We are also interested in the development of a generic screening methodology for nanoparticles, and to identify nanoparticle features which are likely to lead to effects in cells. The present results have been obtained with a set of five silica nanoparticles, four of which were spherical (about 20 nm in diameter) and one of which had an elongated shape (roughly 4 x 20 nm). Size and zeta potential measurements were performed, and the adsorption profiles for the nanoparticles when interacting with each of four model lipid membranes of different composition and net charge were monitored in real time using the quartz crystal microbalance with dissipation monitoring (QCM-D). We found clear differences in adsorption profiles on the model membranes with respect to surface coating, and particle shape. These results were compared to the results obtained when exposing frog cells to the same particles, using a conventional assay detecting cellular damage and cytotoxicity (through cell lactate dehydrogenase (LDH) release) and as well in experiments where the function of frog cells cultured on QCM-D sensors was studied by QCM-D (the method is published in Frost et al., Analytical Biochemistry, in press). In general, there were small effects on the cells.

The results will be discussed in the perspective of establishing (Q)SAR for nanoparticles.

9:40am **BI+AS+BA+NL-TuM6 Using Real-Time Acoustical Sensing by QCM-D to follow Dynamic Processes in Live Cell Morphology and Cell-Surface Interactions**, ***E. Nilebäck***, Biolin Scientific, Sweden, *N. Tymchenko, A. Kunze,* Chalmers University of Technology, Sweden, *L. Enochson,* University of Gothenburg, Sweden, *P. Wallin, J. Gold, S. Svedhem,* Chalmers University of Technology, Sweden, *A. Lindahl*, University of Gothenburg, Sweden

The mechanical properties and morphology of living cells are dynamic and regulated by cell signaling pathways that can be triggered by both external and internal stimuli. The dynamic nature of these cellular shape changes leaves a great potential for real-time techniques to reveal new time-resolved information in addition to microscopy methods based on fluorescence that are typically end-point measurements. By using quartz crystal microbalance with dissipation monitoring (QCM-D), the nano-mechanical properties at the cell-surface interface can be studied. How the cells interact with the surface greatly influences the QCM-D response, particularly at cell adhesion and when the cells undergo morphological changes due to internal or external stimuli.

To explore the potential of acoustically sensing the cell-surface interface in real-time, we have used QCM-D as the main technique in several cell studies:

i) Changes in cell morphology were studied simultaneously by QCM-D and light microscopy as 3t3 and human derived fibroblasts were subjected to the actin disrupting agent cytochalasin D that depolymerizes actin in the cytoskeleton. This resulted in a dramatic change in cell morphology that was reversible upon rinsing and could repeatedly be detected as significant changes in the energy dissipation. [1]

ii) Cell adhesion and cell-surface interactions were studied for human derived chondrocytes as they were subjected to well-defined layers of the glycosaminoglycan (GAG) hyaluronan (HA). HA is present in e.g. extra cellular matrix of cartilage and the chondrocytes could be seen in the QCM-D signal to degrade the GAG layer in 2 hours.

iii) Cell adhesion and fixation studies of 3t3 fibroblasts were performed on silicon dioxide coated surfaces with and without a coating of serum proteins. This revealed that the protein layer greatly affected the QCM-D response from the cells. The later fixation by formaldehyde was performed *in situ* and from the QCM-D data it was shown that the viscoelastic behavior of the cells was to a large extent retained after fixation.

1. Tymchenko, N., Nilebäck, E. et al., *Reversible Changes in Cell Morphology due to Cytoskeletal Rearrangements Measured in Real-time by QCM-D,* Biointerphases, 2012. (1): p. 1-9.

11:00am **BI+AS+BA+NL-TuM10 QCM-D as a Novel Technique to Investigate Nuclear Pore Transport**, ***M. Sorci***, Rensselaer Polytechnic Institute, *R. Hayama, B.T. Chait, M.P. Rout,* Rockefeller University, *G. Belfort*, Rensselaer Polytechnic Institute

A quartz crystal microbalance (QCM-D) is a simple and highly sensitive mass and dissipation sensor which has been used to study interfacial adsorption reactions and conformational changes on a variety of supports in real time. In this paper we aim to apply this technique to gain a better understanding of nuclear transport. In particular, we are investigating the transport of proteins through the Nuclear Pore Complex (NPC), which is the sole mediator of exchange between the nucleus and the cytoplasm in all

eukaryotic cells[1]. Recent publications have further improved our understanding of the architecture and evolutionary origins of this macromolecular gate,[2,3] yet the molecular transport mechanism remains unclear. Transport across the NPC is fast, energy-dependent (to give directionality) and often receptor-mediated. While small molecules pass through the NPCs unchallenged, large macromolecules (>40 kDa) are excluded unless chaperoned across by transport factors collectively termed Karyopherins (Kaps). The translocation of the complexes of Kaps and their cargo proteins/RNAs occurs through the specific affinity and binding between Kaps and particular nuclear pore complex proteins (nucleoporins) called FG-Nups, which share a degenerate multiple-repeated "Phe-Gly" motif. In an attempt to better understand the transport and the selective process under crowding conditions, we immobilized Nsp1 and truncated variations of it onto QCM-D sensors. The binding and unbinding of Kap95, other binding proteins, as well as control proteins (e.g. BSA), was studied in order to investigate specificity, kinetics rate constants, effect of competitive binding. Ultimately we aim to gain sufficient understanding of the molecular scale engineering principles behind nuclear transport to allow us to design the next generation of synthetic selective nanosorters capable of purifying any protein that we desire.

1. Grünwald, Singer and Rout, Nature 2011, 475, 333

2. Alber et al., Nature 2007, 450, 683

3. Alber et al., Nature 2007, 450, 695

11:20am **BI+AS+BA+NL-TuM11 Using QCM-D and Ellipsometry to Determine the Orientation and State of Hydration of Antibodies Adsorbed on a Hydrophobic Surface**, ***C.W. Frank***, Stanford University, *M.E. Wiseman*, DSM Research **INVITED**

Adsorbed antibodies can take several orientations: end-on/fab-up, end-on/fab-down, side-on, and flat-on. Since the accessibility of antigens will depend on the antibody orientation, we have used QCM-D to monitor transient adsorption and have determined the orientation as a function of coverage. In addition, we have used simultaneous QCM-D and ellipsometry to distinguish between the "wet" mass consisting of protein plus coupled water and the "dry" mass consisting only of the protein. Finally, we have applied an alternative protocol for determining the state of hydration using only QCM-D. This involves a D_2O exchange that allows determination of the dry mass. We conclude that the QCM-D signal of proteins in liquids contains a major component from coupled water.

Manufacturing Science and Technology
Room: 202 B - Session MS+AS+BA+BI+PS+TF-TuM

IPF 2013-Manufacturing Challenges for Emerging Technologies: IV. Manufacturing Challenges: The Life Sciences

Moderator: D.G. Castner, University of Washington, L.J. Gamble, University of Washington

8:00am **MS+AS+BA+BI+PS+TF-TuM1 Microfluidics for Chemical Analysis**, ***L. Carr***, *Q. Bai, R. Brennen, S. Post, G. Staples, K. Seaward, H. Yin, L. Martinez, D. Ritchey, K. Killeen*, Agilent Technologies **INVITED**

Chemical analysis is an essential tool for pharmaceuticals, environmental testing, food safety, forensics, energy and many other industries. The need for faster, more accurate and more sensitive measurements continuously pushes the limits of measurement technology and creates opportunities for advances in chemical analysis instruments and applications. One way in which this need can be addressed is by incorporating microfluidic devices in High Pressure Liquid Chromatography (HPLC). Pressure-based microfluidic chips have enabled a new class of reproducible integrated workflow devices that combine sample preparation, enrichment, and HPLC separation *with an integrated ESI/MS (Electrospray Ionization/Mass Spectrometry) interface* for high sensitivity nanoflow Liquid Chromatography-Mass Spectrometry (LC-MS). These devices have most commonly been fabricated using polymer, ceramic, and glass materials but the next generation of higher capacity and throughput microfluidic chips for LC-MS requires materials and structures capable of ultra high pressure operation. In this work, we describe the fabrication and performance of diffusion-bonded metal chips for high performance nano- and microflow LC-MS operation. The microfabrication technology required to make these devices includes semiconductor fabrication standards such as photolithography and thin film deposition, as well as laser ablation, electrochemical etching, and diffusion bonding. These novel metal devices exhibit state of the art performance in resolution and throughput for microfluidic LC-MS chips. These chips are an example of improvements in measurement sensitivity, resolution, speed, and ease of use that have been made possible by utilizing microfluidic devices for chemical analysis.

8:40am **MS+AS+BA+BI+PS+TF-TuM3 Challenges in the Fabrication of Nanoscale Devices for DNA Base Sensing**, ***S. Papa Rao***, *J. Bai, E.A. Joseph, R.L. Bruce, M. Lofaro, M. Krishnan, M. Brink, M. Guillorn, S.M. Rossnagel, Q. Lin, J. Cotte, C. Jahnes, Smith, Gignac, Reuter, Nam, Astier, Wang, Stolovitsky, Goldblatt*, IBM Research Division, T.J. Watson Research Center **INVITED**

The fabrication of integrated circuits with increasingly fine geometries has required the development of advanced process technologies, which can be further refined for the purpose of building devices for biological applications. Applications such as sensing nucleotides in DNA require structures that are of the order of a few nanometers. This talk will focus on the specific challenges encountered in the fabrication of such nano-scale devices – broadly classified into materials-related challenges, unit-process challenges and process integration-related challenges. Issues such as dielectric integrity, metal recrystallization, and materials compatibility with chemistries used down-stream will be discussed. Dimension control during fabrication of ~10 nm sized structures was achieved through intense process development efforts of reactive ion etch and chemical mechanical planarization (both manufacturing-friendly techniques). Device layout issues that affect manufacturability will be presented. Finally, some of the important lessons learned in achieving a high yield of reliable devices through process-integration changes will also be discussed.

9:20am **MS+AS+BA+BI+PS+TF-TuM5 Nucleic Acid Synthesis and Applications**, ***S. Laderman***, Agilent Technologies **INVITED**

The pursuit of perfect and practical *de novo* chemical syntheses of nucleic acids has been the foundation of a broad range of life science accomplishments over many decades in the past. Its further pursuit is enabling a broad range of opportunities many decades into the future. These themes will be elucidated by examining the precedents and improvements enabling high throughput genomics for research and diagnostics through the manufacturing of high quality DNA microarrays and complex pools of long oligonucleotides. Looking forward, new ways to synthesize RNA will enable deeper understanding and improved manipulations of cells, tissues and organisms. At the same time, multiple applications of synthetic biology are motivating additional focus on further advances in flexibly and cost-effectively constructing perfect DNA.

10:40am **MS+AS+BA+BI+PS+TF-TuM9 Single Molecule, Real-Time DNA Sequencing**, ***S. Turner***, Pacific Biosciences **INVITED**

In this talk, I'll convey the story of the development and commercialization of Pacific Biosciences' Single Molecule, Real-Time DNA Sequencing technology. I will start with an overview of the method, how it works, and how if differs from sequencing methods that came before it. I will continue with a discussion of some key technology milestones, with an emphasis on the technological advances in materials engineering and nanofabrication. I'll finish by showing some examples of how this technology has transformed the field of DNA sequencing and genome analysis.

11:20am **MS+AS+BA+BI+PS+TF-TuM11 Opportunities and Challenges in the Biobased Products Manufacturing**, ***J. Flatt***, *S. Bailey, S. Bower, D. Gibson, S. Farah, J. Butler, J. Hannon*, Synthetic Genomics **INVITED**

Biobased production of life's necessities, including food, fuels, chemicals and medicines provides a foundation for sustainable and geographically distributed manufacturing processes. Biobased manufacturing utilizes photosynthetic processes directly through conversion of carbon dioxide and light energy or indirectly through conversion of renewable biomass feedstocks to products. Biological cells (biocatalysts) are the operating systems for these biobased manufacturing processes. Rapid advances in synthetic biology enable the engineering of biocatalysts which can produce a broader range of products than previously possible, at high yields and productivities necessary for achievement of desired economics. Improvements in biocatalysts are achieved through modifications of DNA, which is the software of living systems. Significant advances in the costs, fidelity and speed of DNA synthesis, along with improving understanding of gene function and regulation is enabling the more rapid development of biocatalysts which achieve required performance for commercially viable manufacturing processes. The current state of the art of synthetic biology and technology trends which will impact future development of biobased processes will be discussed. Additional market-specific and process-specific challenges exist, and will be discussed in context of the specific examples taken from manufacture of synthetic vaccines, biobased chemicals and fuels. Recently, Novartis and Synthetic Genomics demonstrated the ability to successfully produce vaccines for prevention of seasonal influenza using synthetic DNA constructs, which significantly reduces the time from

influenza strain identification to production of the vaccine seed. Development of this revolutionary process required significant improvement of the fidelity of DNA synthesis and assembly, which provides insight into the challenge of engineering more complex biocatalysts. On the other end of the spectrum, phototrophic microalgae have great long-term potential to provide a sustainable and alternative source of food and liquid transportation fuels. Phototrophic microalgae can be cultivated using non-potable water on non-arable land. Techno-economic analysis (TEA) and life cycle assessment (LCA) both suggest that significant improvements in biocatalyst productivity and capital cost reduction will be required to achieve competitive economics. Maximum observed algal biomass productivities in the range of 20 to 25 g/m2/day are far lower than generally-agreed upon theoretically-achievable productivities based upon the actual solar energy available. Improvement of photosynthetic efficiency in mass culture is required for economical algal-based processes. Limited availability of light in mass culture also limits the maximum achievable cell density, which results in increased downstream processing costs. The challenges of “dilute solution economics” associated with commercial algae production and potential biological and engineering solutions will be discussed.

Applied Surface Science
Room: 204 - Session AS+BI-TuA

Forensic Science, Art and Archaeology (2:00-3:20 pm)/Quasicrystals and Complex Metal Alloys (4:00-6:00 pm)
Moderator: J.A. Ohlhausen, Sandia National Laboratories, R. Opila, University of Delaware, S.J. Pachuta, 3M Company

2:00pm **AS+BI-TuA1 Validation of Ultra-Trace Biological Agent Sample Matching Using NanoSIMS**, ***P.K. Weber***, *M.L. Davisson, C.E. Ramon, S.P. Velsko*, Lawrence Livermore National Laboratory **INVITED**

The threat associated with the potential use of radiological, nuclear, chemical and biological materials in terrorist acts has resulted in new fields of forensic science using state-of-the-science analytical techniques. One such method is high spatial resolution secondary ion mass spectrometry (SIMS) performed with a Cameca NanoSIMS 50. This instrument allows us to extract quantitative trace element and isotopic information for forensic purposes at a resolution of ~100 nanometers. With this capability, target particles with contaminated or ultra-trace samples can be analyzed. Here we present a general validation scheme and extend it to the analysis of small numbers (3-10) of anthrax spores. The scheme tests the hypothesis that two samples were produced in the same laboratory by the same process. This test is generally known as "sample matching", though the term "match" is not used. Instead, the test uses receiver-operating characteristics (ROC) curves derived from test samples to generate a likelihood ratio that is combined with other data relating to the hypothesis. For our work, we are using the elemental composition of single anthrax spores as evidence.

To evaluate the sample matching test we used a well-defined statistical design to generate *B. anthracis* samples that are representative of agents made by benchtop scale processes that might be encountered in terrorism events. We used the NanoSIMS to profile the elemental composition of individual bacterial spores. Between 8 and 20 elements were monitored. The dynamic range of the analyses was on the order of one million. An objective metric for the "closeness" of two samples was defined in terms of the differences between elemental concentrations. A ROC curve for the same lab-same process and same batch hypothesis tests were calculated based on the difference metric. The ROC curves for averages of small numbers of spores (3-10) were determined, and were compared to bulk elemental analysis.

Our results support the following conclusions: The average elemental composition of two samples containing a small number of spores (3 - 10) can have reasonable inferential power for determining if the samples were made in the same laboratory using the same process. The ROC curve for determining if two samples originate from the same batch offer less inferential power than those for the same lab - same process test. ROC curves for NanoSIMS-based comparisons are optimized by using a particular set of elements, but the dependence on element set is relatively weak.

2:40pm **AS+BI-TuA3 Characterization of Foreign Material from Buried Interfaces in the Medical Device Industry**, ***W. Theilacker***, *A. Belu, A. Burand*, Medtronic, Inc.

This presentation will highlight the use of surface analysis methods for the characterization of buried interfaces on medical devices. Manufacturing of medical devices requires the highest level of quality to ensure optimal device performance and patient safety. Pacemakers, leads, and cardiovascular products often contain components and sub-systems that are potted in an overlayer of semi-transparent material including silicones, urethanes, cyanoacrylates, and epoxies. This process serves to isolate electrical feedthroughs and contacts, fill gaps and voids, and to create water tight seals. Occasionally surface residues from raw materials, manufacturing processes, cleaning, and handling become trapped at this interface and are often not detected until later in the build process. Their presence could degrade performance, prevent adhesion, generate corrosion, or simply result in a cosmetic blemish. Identifying the elemental and chemical composition of foreign material from buried interfaces is a very difficult task and often requires a multi-technique approach. In this study, titanium, polycarbonate, and silicon-based substrates were coated with a thin layer of commonly observed inorganic and organic manufacturing residues and buried under overlayers (<100 nm) of various organic materials. Both non-destructive (e.g., confocal Raman spectroscopy) and destructive analysis (e.g., ion beam sputtering along with XPS and TOF-SIMS) were applied to gain insight into the chemical composition of the interfacial regions.

3:00pm **AS+BI-TuA4 Forensic XPS Characterization of Surface-Modified Textile Fibers**, ***B. Strohmeier***, Thermo Fisher Scientific, *C. Deeks*, Thermo Fisher Scientific, UK, *R. Blackledge*, Forensic Chemist Consultant

Despite its many advantages and unique capabilities as a surface analytical technique, X-ray photoelectron spectroscopy (XPS) has not been widely used in forensic science for the examination of specimens gathered at the scene of a crime. Reasons for the lack of forensic XPS studies in the past include: 1) the absence of standard forensic XPS methods and standard reference materials for comparison to real world samples; and 2) the historical long analysis times (e.g., hours per sample), relatively large analysis areas (e.g., several square millimeters), and the relative high cost of XPS instrumentation compared to more common forensic analytical tools such as scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM/EDS), Fourier transform infrared (FT-IR) microscopy, and Raman microscopy. Advances in XPS instrumentation over the last few decades, however, have improved typical analysis times to minutes per sample and analysis areas down to the range of tens to hundreds of micrometers. In addition, recently developed argon cluster ion sources now allow depth profiling of organic species with minimal ion beam damage, thus preserving the chemical information available from XPS. Therefore, XPS has increased potential for new applications in forensic science. One such area is the forensic surface characterization of textile fibers. White cotton fibers are so common and have so few visual distinguishing features that they are largely ignored by forensic scientists at crime scenes. However, most fabrics today have received one or more types of organic-based surface-modification treatments to provide stain resistance, permanent press characteristics, and/or waterproof properties. This presentation will discuss a proof of concept study on the use of XPS to differentiate individual textile fibers based on their surface chemistry. Materials examined in this study included swatches, threads, and individual fibers from a variety of different cotton and polyester/rayon fabrics before and after receiving one of several different commercial textile surface-treatments. Results indicated that small spot XPS combined with argon cluster ion depth profiling can: 1) distinguish among various untreated textile materials based on differences in surface chemistry resulting from their specific manufacturing process; and 2) distinguish between otherwise identical appearing fibers by differences in the textile surface treatment applied. These results demonstrate that XPS has the potential for identifying and distinguishing textile fibers found at crime scenes.

4:00pm **AS+BI-TuA7 Surface Properties and Complexity of Al-based Intermetallics**, ***J.-M. Dubois***, CNRS, France **INVITED**

Quasicrystals represent the ultimate state of lattice complexity in a crystal. Shechtman, who discovered quasicrystals,[1] was awarded a Nobel Prize in Chemistry in 2011 for having led to a revolution in the way ordered solids are now understood in materials science. The talk will focus on a specific series of compounds, namely Al-based complex metallic alloys (CMAs) which comprise a significant number of crystalline compounds of changing lattice complexity, according to composition, and yield few icosahedral compounds that are thermodynamically stable and may be prepared into various sample shapes that allow for the measurement of surface physical properties.

Surface energy (γ_S) is one of the few fundamental properties of condensed matter: it defines the equilibrium shape of a crystal, it determines the interfacial behavior of any piece of liquid or solid against another body, etc. The talk will summarize a number of attempts to estimate the surface energy of a large variety of CMAs, including the stable, icosahedral Al-Cu-Fe and Al-Pd-Mn quasicrystals.

Pin-on-disk experiments, after appropriate calibration, lead to reliable data that fall in the range $0.5 < \gamma_S < 0.8$ Jm^{-2} for these compounds.[2] The average value of γ_S is about one half that of pure aluminum (γ_S = 1.15-1.2 Jm^{-2}), and less than a quarter that of iron (γ_S = 2.2-2.4 Jm^{-2}). It is consistent with the low wetting behavior and reduced adhesion force against hard steel observed in high vacuum for these quasicrystals. Correlation to specific features of the electronic density of states will be emphasized, in line with the varying complexity of the studied CMA compounds. Potential applications in high vacuum technology will be addressed.

References:

1- D. Shechtman, I. Blech, D. Gratias and J.W. Cahn, Phys. Rev. Lett., 1984, **53-20**, 1951.

2- E. Belin-Ferré and J.M. Dubois, Int. J. Mat. Res., **97** (2006) 7.

4:40pm **AS+BI-TuA9 Structural Investigation of the (001) Surface of Al_5Co_2, *M. Meier*, *J. Ledieu, M-C. de Weerd, E. Gaudry, V. Fournée*,** CNRS-Université de Lorraine, France

Complex metallic alloys (CMAs) like quasicrystals and approximants are being considered as low-cost alternative materials for heterogeneous catalysis [1,2]. It relies on the so-called site-isolation concept in which the catalytic performance of a material is ascribed to small and well-separated atomic ensembles containing an active transition metal (TM) element at the crystal surface. Such atomic ensembles must be stable under reaction conditions, which in turn depend on the chemical bonding and the crystal structure of the intermetallic compound. $Al_{13}TM_4$ compounds have been identified as promising candidates for the heterogeneous hydrogenation catalysis [2, 3]. Here we focus on a related CMA system, the Al_5Co_2 crystal, which is also considered as a quasicrystalline approximant.

As a first step towards the understanding of the catalytic properties of this new phase, an atomic scale description of its surface is mandatory. First, a single crystal has been grown using the Czochralski method and oriented perpendicular to its [001] axe. The surface structure investigated under ultrahigh vacuum conditions by low energy electron diffraction and scanning tunnelling microscopy (STM) exhibits a $\sqrt{3}x\sqrt{3}R30°$ reconstruction. According to the bulk model, two types of atomic layers are stacked along the [001] direction: either pure Al puckered (P) layers or flat (F) layers containing both Al and Co atoms. The step height measured by STM indicates that only one type of plane appears as surface termination. Atomically resolved STM images show small triangular atomic ensembles separated by 13 Å from each other and consisting of 3 bright protrusions. Such local configurations can only be interpreted as a reconstructed P layer where a fraction of Al atoms are missing. First-principles calculations using density functional theory (DFT) confirm that P layers are preferred terminations compared to F layers. Calculated surface energies for various surface models, along with the corresponding simulated STM images, show that the $\sqrt{3}x\sqrt{3}R30°$ reconstruction is due to a specific set of missing Al surface atoms. Finally, a very nice agreement is obtained between simulated and experimental STM images, thus confirming the surface model. Other surfaces of interest for catalysis are currently being studied, namely the (100) and the (2-10) surfaces, together with their chemical reactivity towards small molecules of interest (O_2, CO, acetylene,...).

[1] T. Tanabe, S. Kameoka, A. P. Tsai, Appl. Catal., A 384, 241 (2010).

[2] M. Armbrüster, K. Kovnir, M. Friedrich, *et al.* Nat. Mater. 11, 690 (2012).

[3] J. Ledieu, É. Gaudry, L. N. Serkovic Loli, *et al.* Phys. Rev. Lett. 110, 076102 (2013).

5:00pm **AS+BI-TuA10 Temperature-Dependence of Ag Film Roughness and Interlayer Spacings During Deposition on Complex Al-Pd-Mn Surfaces: Comparison with Periodic Substrates**, *B. Ünal,* Massachusetts Institute of Technology*, J.W. Evans,* ***P.A. Thiel***, Ames Laboratory and Iowa State University

The morphology of thin metal films deposited on metal substrates is often dominated by kinetic rather than thermodynamic factors . These factors can assessed by studying film characteristics as a function of deposition temperature. In this study, we report a comparison of the roughness of thin Ag films deposited on surfaces of a quasicrystal (five-fold icosahedral Al-Pd-Mn), an approximant of this quasicrystal, and low-index Ag surfaces, at temperatures below and up to ambient. Kinetic effects lead to an increase in roughness with increasing temperature for the Al-Pd-Mn substrates, but a decrease in roughness over the same range on Ag(111) and Ag(100). The nature of these effects is discussed. In addition, we observe that interlayer spacings in the film depend upon layer height, for the Al-Pd-Mn substrates. A useful refined definition of roughness for a system with variable interlayer spacing is addressed.

5:20pm **AS+BI-TuA11 Study of Quasicrystal / α - Mg Eutectic Structure in the Mg-Cd-Yb System by EBSD**, ***A.P. Tsai***, Tohoku University, Japan

A pseudo-binary phase diagram composed of iQc (icosahedral quasicrystal) and α-Mg in Mg-Cd-Yb system reveals a eutectic reaction at $Mg_{68}Cd_{24}Yb_8$. The alloy with eutectic composition prepared by slow cooling shows irregular eutectic structure of QC and α phases. In terms of interface stability, the iQc / α interfaces are realized to be most stable since eutectic structure contains largest area of interface. This study is aiming at understanding an essential question; “how does a quasiperiodic lattice match a periodic lattice ?” The other challenging topic is the application of EBSD (Electron Back Scattering Diffraction) for the first time to study microstructure of a quasicrystalline material.

In X-ray diffraction patterns, a number of main peaks of iQc coincide with those of α phase, indicating good lattice matches between two phases. For examples, basal plane and prismatic plane of α phase have the similar lattice spacing to 2-fold symmetry plane and 5-fold symmetry plane, respectively. EBSD analysis revealed that the growth direction of iQc-α eutectic is ,,2f .-iQc. // ,,1 0 ,1. 0 .-Mg. and a number of orientation relationships between QC and α phase have been verified. Furthermore, a number of directions normal to the planes of iQc coincide to those normal to the planes having similar lattice spacing of iQc in the α phase. The interface stability is likely due to good lattice matches between iQc and α phase.

5:40pm **AS+BI-TuA12 Plasmonic Quasicrystal Lattices**, ***T.W. Odom***, Northwestern University

Quasicrystals are ordered materials that do not have translational symmetry but form stable structures with rotational symmetries higher than periodic materials. Artificially structured high-symmetry lattices based on quasicrystalline structures have recently been generated using nanoparticle building blocks and nanoholes. The design of quasicrystal arrays with subwavelength spacings is especially important in photonics since such symmetries can result in full band gaps in photonic crystals and omnidirectionally trap light in patterned photovoltaic devices. This talk will describe a novel nanofabrication method—moiré nanolithography—that can fabricate subwavelength lattices with high rotational symmetries over wafer-scale areas. By exposing elastomeric photomasks sequentially at multiple offset angles, we could create nanoscale arrays with rotational symmetries as high as 36-fold, which is three times higher than quasiperiodic lattices (≤ 12-fold) and six times higher than two-dimensional periodic lattices (≤ 6-fold). We transferred these patterns into noble metal films to generate plasmonic quasicrystal lattices, which show unique optical properties. A new scheme required for indexing these new plasmonic modes will be discussed.

Biomaterial Interfaces
Room: Hall B - Session BI-TuP

Biomaterials Interfaces Poster Session

BI-TuP2 Monocyte Adhesion to Protein Functionalized Nanopatterns, ***A.S. Andersen***, *D.S. Sutherland*, Aarhus University, Denmark

Through a biofunctionalized nanopattern proteins are presented in circular nanopatches, which can range from 66nm-3µm in size. These protein nanopatches are used to study cell binding, specifically in regards to ligand clustering. Monocytes are the precursors for our body's macrophages, the scavenger cells, which for example help during inflammation and to remove apoptotic cells. Monocytes are found in the blood and needs to be recruited to sites of inflammation. This happens in four stages, rolling, binding, diapedesis and migration. The focus of this research is in the first two stages. During binding an integrin, LFA1, on the monocyte binds to its ligand, ICAM1, on the epithelial cells and it is known that these form focal adhesions (FA). The size of the FA, needed to get a strong binding, is not known. This research uses a nanopattern (1), biofunctionalized through a serial protein deposition (2) mimicking FA ICAM1 patches. The binding of THP1 cells to 100-800nm sized ICAM1 nanopatterns will be shown. It illustrates a cut off in size where the cell binding disappears indicating that there is a crucial size of FA for monocytes to adhere.

Further, results showing a protein nanopattern made inside a microfluidic channel are presented. The nanopattern consists of circular gold covered holes 800nm in diameter, in a PLL-g-PEG covered SiO2 surface. The gold holes have been biofunctionalized through a serial protein deposition which gives an oriented antibody pattern, with the possibility to change to any protein with a FC domain attached. The microfluidic setup will allow for cell studies under flow and opens up the opportunity to mimic the flow conditions found in the blood stream during cellular adhesion, which have been shown to be an important factor in monocyte adhesion.

1: Jenny Malmström, Brian Christensen, Hans P. Jakobsen, Jette Lovmand, Rasmus Foldbjerg, Esben S. Sørensen, and Duncan S. Sutherland. Large Area Protein Patterning Reveals Nanoscale Control of Focal Adhesion Development. Nano letters, Vol 10, 686-694, 2010.

2: Stine H. Kristensen, Gitte A. Pedersen, Lene N. Nejsum and Duncan S. Sutherland. Nanoscale E-Cadherin Ligand Patterns Show Threshold Size for Cellular Adhesion and Adherence Junction Formation. Nano Letters, 12(4), 2129-2133 2012.

BI-TuP3 Ultrasound Imaging, Gamma Scintigraphy and HIFU Therapy with Perfluorocarbon Loaded Iron-Silica Nanoshells, ***A. Liberman***, *Z. Wu, C. Barback, R. Viveros, S.L. Blair, D. Vera, L.G. Ellies, R.F. Mattrey, W.C. Trogler, A.C. Kummel*, University of California San Diego

The reported positive margin rate from wire localized excisions of breast cancers is approximately 20-50%; however, by preoperatively injecting a radioactive seed into the tumor under CT guidance, the excision rate is halved because the surgeon can constantly reorient the dissection to place the seed in the center of the specimen. Unfortunately, radioactive seed localization has several safety challenges, only single focus can be localized, and incisions are required to implant the seeds, so it is rarely employed. As an alternative, gas-filled hollow Fe-doped silica particles have been developed, which can be used for ultrasound-guided surgery even 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 and iron ethoxide, which forms a rigid, nanoporous shell upon calcination. The nanoshells are filled with perfluoropentane vapor or liquid. The flourous phase is contained within the shell due to its extremely low solubility in water. *In vivo* particle longevity studies have been performed in tumor bearing mouse models show signal presence up to 10 days post injection. To study biodistribution, nanoshells were functionalized with DTPA and radiolabeled with ^{111}In and then imaged by γ-scintigraphy. Scintigraphic imaging and γ-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. The nanoshells break under acoustic excitation to release gas pockets which increase acoustic energy absorption and reduce acoustic cavitation threshold. 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 (mins) and high risk during continuous perfusion. Preliminary *in vivo* HIFU ablation studies show that 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 hrs after administration. This cavitation caused liquification within the focal volume of the HIFU which contained the nanoshells within seconds. This may potentially allow for a larger area to be ablated in less time with less power.

BI-TuP4 Development of Nanofibrous Meshes as Smart Dressings for the Healing of Chronic Wounds, ***M. Abrigo***, *S.M. McArthur, P. Kingshott*, 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. Chronic wound care currently focuses on dressings capable of preventing microbial infiltration and keeping a balanced moisture and gas exchange environment. The design of 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 wound care.

Polymeric nanofibrous meshes are good candidates as wound dressings and cell scaffolds due to their high surface area, micro-porosity and non-woven structure. Electrospinning is used for the fabrication of these structures because it is a simple, cost-effective and reproducible process. Moreover, electrospinning enables fibres of synthetic and natural polymers to be combined as multifunctional dressings capable of addressing a range of wound challenges.

In this study, a range of different synthetic polymers (Poly-lactic acid, Poly-glycolic acid and Polycaprolactone) have been blended and the parameters of the electrospinning process (such as spinning rate and electric field intensity) optimized to achieve a nanofibrous membrane. The morphological properties of the electrospun meshes have been analysed by three-dimensional optical profiler, Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). As the first step to understand microbial infiltration and control in wound dressings, a number of studies have been 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.

BI-TuP5 Lipid Interactions with Plasma Polymers, ***H.J. Askew***, *S.M. McArthur*, Swinburne University of Technology, Australia

The cell membrane encases and protects cellular components and plays an important role in transport, signalling and disease . Studying membrane behaviour is a challenging task due to the complexity and scale on which these processes occur. Supported lipid bilayers (SLBs) have provided researchers with stable and reproducible platforms to recreate cell membrane environments. The planar structure of the model means a variety of patterning techniques can be employed to recreate membrane architecture on both a micro and nanoscale. In particular pre-patterned substrates are of great interest as they eliminate complications associated with preserving membrane integrity during patterning. Plasma polymers provide a versatile method of creating thin films with a variety of different surface chemistries. In this work we explore the behaviour of plasma coatings in aqueous conditions and the use of plasma films for creating patterned SLBs using vesicle collapse. A variety of micropatterned surface chemistries were formed using commonly used plasma polymers such as allylamine and acrylic acid combined with standard UV photolithography techniques. Characterisation of film behaviour and bilayer formation was conducted using a variety of techniques including ellipsometry, quartz crystal microbalance with dissipation (QCM-D), confocal microscopy and atomic force microscopy (AFM). This study adds to the currently limited literature considering plasma film behaviour in aqueous conditions. Plasma coatings provide a versatile technique for micropatterning SLBs and have advantages over other commonly used techniques such as microcontact printing which suffers from PDMS contamination. Further optimisation of the plasma patterning process may yield increased resolution and chemistries to aid the development of increasingly complex SLB systems.

BI-TuP6 Pseudomonas Aeruginosa Biofilm Formation Mechanisms on Highly Ordered Micro and Nano-sized Colloidal-based Patterns, ***H. Pingle****, P.Y. Wang,* Swinburne University of Technology, Australia*, C.B. Whitchurch,* University of Technology Sydney, Australia*, P. Koegler, S.M. McArthur, P. Kingshott*, Swinburne University of Technology, Australia

Pseudomonas aeruginosa is an opportunistic pathogen with life threatening complications for hospitalised patients needing catheters or other medical devices when it forms biofilms on the surface of that device. Each year almost 16,000 catheters related blood stream infection cases are found in USA only, with estimated mortality rates ranging from 12% to 25% even with use of uncompromising antibiotics. Some research has shown that extra-cellular DNA is involved in *Pseudomonas aeruginosa* biofilm formation but the actual part it plays in initiating attachment and how it helps bacteria to form multicellular biofilms is unknown. New surfaces are therefore seriously needed to understand the exact mechanisms and prevent biofilm formation. We use a novel approach for making chemical micro and nano patterns on material surfaces with the help of self-assembled colloidal particles used as masks for creating advanced material surfaces. Recently we have prepared binary colloidal assembly of different crystal structure over a wide range of size ratios (Y=small/large) from 0.01 to 0.2 by tuning Y during assembly and characterised the surface using Scanning Electron Microscope (SEM). We found that zeta potential and size ratio are critical for self-assembly crystal formation. When zeta potential over -30 mV resulted in crystal structure formation. Beyond this range, disordered structure or particle-particle adsorption was found. The crystals are used as masks against gold and plasma polymer deposition to create chemical patterns on the surface that are used for immobilising of eDNA to study how *Pseudomonas aeruginosa* attaches to surfaces and form biofilms.

BI-TuP7 Quantification of the Adhesion Strength of the Diatom *Navicula perminuta* in a Microfluidic Assay, ***M. Alles****, C. Christophis,* University of Heidelberg, Germany*, M.E. Callow,* University of Birmingham, UK*, M.H. Grunze,* University of Heidelberg, Germany*, A. Rosenhahn*, Ruhr-University Bochum, Germany

In recent years Fouling-Release (FR) technologies have been significantly improved and can be considered as an environmental benign approach against marine biofouling [1]. FR coatings refer to those coatings on which microorganisms adhere only weakly allowing their release by low shear stresses present e.g. at the hull of a cruising ship. To study cell adhesion strength on different substrates quantitatively, a microfluidic shear force assay was developed [2-3]. After an attachment phase, the adhesion strength of cells can be measured by detaching them from substrates using a stepwise increased flow across 6 orders of magnitude starting with very low shear forces of 0.01 dyn·cm^{-2}. With this device we can determine both, the fraction of adherent cells and the critical shear stress which is necessary to remove 50% of the adherent cells. Diatoms are frequently observed biofoulers and prevalent on fouling-release coatings commercially used [4]. In the presented work we tested the effect of different incubation conditions and attachment geometries on the attachment strength of the marine diatom *Navicula perminuta*. Furthermore we used chemically different substrates to determine if adhesion strength of *Navicula* is changed on potential foul-release chemistries. By this microfluidic approach, inert chemistries can readily be discriminated from surfaces with low foul release properties and the high sensitivity allows revealing even subtle differences in adhesion caused by a change in surface properties.

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BI-TuP9 Bacterial Deposition of Patterned Cadmium Sulfide Thin Films, ***K.E. Marusak****, S. Payne, Y. Cao, L. You, S. Zauscher*, Duke University

The need for new energy harvesting techniques increases, and research in photovoltaics is becoming more and more essential. In particular, there has been a growing research effort focused on "green" manufacturing techniques, including the use of bacteria to precipitate semiconducting nanoparticles. We argue that *E. coli* has tremendous potential in the fabrication of patterned cadmium sulfide thin films for solar cell applications. Here we capitalize on the ability of genetically engineered *E. coli* to precipitate cadmium sulfide nanoparticles, through the expression of the Treponema denticola cysteine desulfhydrase gene,[1] and we show that these genetically engineered *E. coli* have the ability to form patterns and monolayers on silica, glass, and indium tin oxide. Furthermore, we discuss the properties of the deposited cadmium sulfide nanoparticles and films, where we have used X-ray photoelectron spectroscopy, FTIR spectroscopy, X-ray diffraction, and scanning electron microscopy.

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BI-TuP10 Lipid Membranes as Dynamic Templates for the Assembly of Inorganic Nanoparticles, ***P. Bao****, G.R. Heath, J. Roth, B. Johnson, M. Cheetham, R.J. Bushby, S.D. Evans*, University of Leeds, UK

Supported lipid bilayers have found widespread use a model system for the investigation of basic properties of cell membranes, as well as for the development of diagnostic assays and in biosensing [1-3]. The potential of supported lipid bilayers however is still not fully realised considering the possibility of fine tuning the surface charge, fluidity, and organisation at the molecular level. In this work we have been interested in using the dynamic nature of the planar membrane as a substrate to support the crystallisation of monolayers gold nanoparticles. Two different methods of crystal formation have been investigated. In the first negatively charged gold nanoparticles were attached to a neutral lipid bilayer via cholesterol anchors and concentrated via the application of an electric field within the plane of the membrane [4-8]. This resulted regions of high nanoparticle density. We describe results of electric field annealing and the role of nanoparticle concentration on the structures formed. In the second approach we first created a bilayer displaying a phase-separation, into liquid ordered and discorded regimes and containing a small fraction of positively charged lipid. Interestingly the gold nanoparticles spontaneously assembled on the liquid ordered regimes to form quasi-crystals of nanoparticles.

The presentation will describe our combined fluorescence microscope and atom force microscope (AFM) studies on these systems and the role of temperature on assembly formation as well as the mechanism related to the crystallisation. Our results may inspire a wider application lipid bilayers as dynamic structures for the directed assembly of inorganic materials.

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BI-TuP14 Biocompatible Hydrogel Materials - Surface Properties and Deposition Comparison of Commercially Available Contact Lenses, ***K.A. Wygladacz****, D.J. Hook, S.E. Norton*, Bausch and Lomb

Hydrogel contact lenses are ophthalmic devices designed to correct refractive errors. Wettability, modulus, friction, oxygen permeability, and topography are some of the factors that influence lens comfort and performance. In addition, elimination of deposition of proteins and lipids on the lens surface from the tear fluid is of particular interest as it may influence contact lens surface wettability and impact comfort negatively. Thus, the surface chemistry and morphology of a durable and biocompatible hydrogel material should be carefully fashioned.

The objective of this research was to understand the properties of modern daily disposable contact lens materials. The surface composition, morphology, wettability and protein/lipid uptake of worn and unworn nesofilcon A and delefilcon A hydrogels were examined by X-ray Photoelectron Spectroscopy (XPS), Atomic Force Microscopy (AFM), and Captive Bubble (CBCA). Lenses from 5 healthy adults were examined after 4 hours of continuous wearing. A Dimension ICON AFM was used to characterize the unworn and worn hydrogels. Topography, peak to valley, and roughness (RMS) were recorded. AFM phase lag was used to evaluate lipid/protein deposition. Multipoint XPS spectral analysis was performed to establish the spatial distribution of elements over a large area of the hydrogel. CBCA was done to compare the wettability of unworn lenses.

AFM and XPS characterization revealed significant surface chemistry and morphology differences between worn and unworn lens materials. XPS mapping showed a uniform distribution of the identified elements on the

surface of unworn nesofilcon A and also detected the presence of a coating on delefilcon A. Unworn nesofilcon A exhibited a smooth featureless surface morphology with RMS of 1.9 ± 0.2 nm while unworn delefilcon A showed clear presence of a branched surface coating (RMS = 14.2 ± 5.5 nm) with peak to valley as deep as 61.4 ± 18.8 nm. It was established that the wear process changes the contact lens material morphology. The changes observed in the case of worn nesofilcon A were minor, while those observed for worn delefilcon A were quite pronounced. Both daily disposable materials attracted lipid/protein deposits. The topography of worn nesofilcon A was uniform and it was not altered by wear. The branched surface coating of delefilcon A collapsed during 4 hours of wear on eye and was no longer detected by AFM. In addition, delefilcon A attracted more deposits than the nesofilcon A. Topography and phase lag AFM imaging of worn deleficon A did not detect any areas that would be lipid/protein deposit free. In terms of stability and lipid/protein deposition nesofilcon A was superior.

BI-TuP15 Nanoscale Topographical Control of Graphene Architecture by Replication of DNA Nanostructures, ***Y.K. Moon***, Sungkyunkwan University, Republic of Korea

Graphene is a very fascinating material because of its unique mechanical and electronic properties. One of the major challenges for graphene is to control its electronic structure in a designed manner for various device applications. To control the electronic structure and unit size of graphene nanostructures, various approaches have been reported, including fabrication of graphene nanoribbons, chemical functionalization of graphene, control of strain applied to graphene by stretching or bending and nanoscale control of three-dimensional (3D) topography of graphene. Among these, the 3D topographical control of graphene showed interesting phenomena such as a pseudo-magnetic field, which was observed in 3D strained graphene on Pt nanobubbles by scanning tunneling microscopy. The 3D topographical control of graphene at the nanoscale level is quite difficult because graphene intrinsically prefers a two-dimensional (2D) structure. Although graphene with local 3D topography was reported to exist in the form of nanobubbles on a Pt (111) surface, ripples on CVD graphene, and corrugated structures on double strand deoxyribonucleic acids (ds-DNAs), there are limits to the geometrical shapes that can be constructed.

It is not possible for graphene itself to produce the designed 3D structures except by creating artificial defects in graphene. Designed templates with nanometer-scale precision are thus required to make various 3D graphene structures in a controlled manner. DNA nanotechnology has provided a platform to construct artificially designed nanostructures which were self-assembled with precisely controllable and programmable nanoscale features with the aid of oligonucleotide recognition. Here, we demonstrate that the nanoscale 3D topography of graphene can be controlled in a designed manner by using artificially designed DNA nanostructures with a high degree of geometrical freedom. Two DNA nanostructures, a one-dimensional (1D), five-helix ribbon (5HR) structure and a 2D double-crossover (DX) lattice, were self-assembled in a solution during annealing. After formation of DNA nanostructures, the samples were deposited on a mica surface. CVD graphene, which was grown on a Cu foil, was transferred onto the DNA nanostructures on the mica surface; during this process, graphene nanostructures were successfully replicated from DNA nanostructures. After the successful production of the designed 3D topography of graphene replicated from DNA nanostructures, we further studied its thermal stability. The influence of temperature on its topography and electrical properties was verified by atomic force microscopy (AFM) and a four point probe, respectively.

BI-TuP16 The Effects of Glycation on Serum Proteins' Affinities for Hemin, ***A.R. Mercer-Smith***, *M.S. Johal*, Pomona College

Non-enzymatic glycosylation is the process by which sugars covalently bond to proteins, potentially altering their structure and function. We investigated the change in affinity of physiologically-relevant proteins for hemin, a small iron containing molecule when it was incubated for two weeks with three sugars: glucose, fructose, and glyoxal. The formation of protein-heme complexes was measured using a Quartz Crystal Microbalance (QCM). We hypothesize that as the protein's exposure time to sugar increases, less hemin will bind to the protein. A decrease in the protein's binding affinity for hemin can negatively impact the protein's ability to transport hemin, which can even lead to free hemin in the blood. Free hemin may lead to higher rates of bacterial infection as some bacteria may use it as a micronutrient.

Applied Surface Science
Room: 204 - Session AS+BI+IS-WeM

Ambient Ionization Mass Spectrometry
Moderator: C. Szakal, National Institute of Standards and Technology, K. Artyushkova, University of New Mexico

8:20am **AS+BI+IS-WeM2 Rapid Evaporative Ionization Mass Spectrometry - Principles and Applications**, *Z. Takats,* Imperial College, London, ***J. Balog***, MediMass Ltd., Hungary **INVITED**

Development of ambient ionization methods lifted some of the constraints on the applications of mass spectrometry regarding sample pre-treatment and accessibility. However, even these techniques failed to offer a general solution for in-vivo analysis. Rapid Evaporative Ionization Mass Spectrometry (REIMS) has been developed to fill this gap and bring metabolic/lipidomic phenotyping into interventional medical environment. Origins of REIMS technique were based on the observation that thermal evaporation of tissues during surgical intervention produces gaseous ions corresponding to complex lipid species. Furthermore, these complex lipid fingerprints were found to show excellent histological specificity, similarly to those obtained by MALDI or DESI. Following the development of REIMS-based intra-surgical tissue identification technology, the mechanism of the technique was studied in details, and a wide variety of further applications were proposed. Observations strongly suggest that the REIMS technique – similarly to sonic spray ionization – transfers pre-formed ions from solution to gas phase. Electric current and power setting studies revealed minor dependence of the ionization efficiency on the AC frequency, while increasing power (and hence current) settings improved ion yield in the studied ranges. Studying the effect of atmospheric interface settings led to the conclusion that gaseous ionic species detected in the mass spectrometer are formed in the intermediate vacuum regime via cluster-surface collision phenomena. The assumption was further supported by cluster pick-up experiments where various parts of the ion optics were labelled with low volatility compounds (Rhodamine 6G, arginine) and surface re-ionization was studied during REIMS process. Based on these observations, a new type of atmospheric inlet was built, featuring a target surface for surface-induced dissociation of large molecular clusters accelerated by free jet expansion. The ions formed on collisions are collected by a ring electrode trap which is coupled to the ion optics of the mass spectrometer. Based on the results of mechanistic and earlier surgical studies, a number of new applications were developed ranging from the analysis of arbitrary liquid samples through identification of bacterial strains to imaging analysis.

9:00am **AS+BI+IS-WeM4 A Microplasma VUV Photoionization Source for Ambient Mass Spectrometry**, ***J.M. Symonds***, *R.D. Gann, F. Fernández, T.M. Orlando*, Georgia Institute of Technology

Microplasma ionization sources have been shown to be simple, effective tools for ambient mass spectrometry. Microplasmas have the advantages of being cheap to operate and manufacture, and require only modest gas flows and power sources. One of the challenges in ambient mass spectrometry is to produce sample ions from a wide variety of sample molecules without excessive fragmentation. Due to the chemically-specific nature of ionization, this remains a challenge for any new source. In this work we attempt to mitigate both of these problems by using high energy photons to ionize our samples. We have created a microplasma source that employs a mixture of neon and hydrogen to produce vacuum ultraviolet (VUV) light which can ionize samples at atmospheric pressure. Traditionally, VUV light has been both difficult and expensive to produce, which limits its use for applications like ambient mass spectrometry. With the development of our microplasma VUV source, we are able to take advantage of the VUV photon's capability as a broadly-applicable, low-fragmentation photoionization source, while retaining the low cost and simple operation which makes ambient mass spectrometry so appealing. By combining this ionization technique with laser desorption, we investigate the use of this source for mass spectrometric imaging.

This work was supported by the National Science Foundation under award number 0923179.

9:20am **AS+BI+IS-WeM5 Advances in Pulsed-Plasma Sources for Surface Analysis by Ambient Mass Spectrometry**, ***J.W. Bradley***, *K. McKay, A. Bowfield,* University of Liverpool, UK, *T.L. Salter,* National Physical Laboratory, UK, *J.W. Walsh,* University of Liverpool, UK, *M.R. Alexander, D.A. Barrett,* University of Nottingham, UK, *I.S. Gilmore*, National Physical Laboratory, UK

The potential benefits of using atmospheric pressure "cold" plasma sources as a means of both desorption and ionisation of material in ambient mass spectrometric analysis of surfaces has been recognized by a number of researchers worldwide. Plasma sources include dielectric barrier jets (PADI [1] and LTP [2]) operating at mid-frequency and also RF corona needle discharges.

Here we develop further strategies to pulse modulate such sources (jet and needle) and investigate the influence of duty cycle on the production of chemical species in the source plasma and the composition of the ionised desorbed species from a range of test surfaces (polymeric, pharmaceutical and biological). For the plasma plume study we use a time resolved (5 μs) Hiden Analytical molecular beam MS (HPR-60) unit, while detailed information on the spatial distribution of surface species from the chosen material samples was done using a Thermo Velos LTQ Orbitrap MS.

The influence of source-sample and sample-instrument distances on the signal intensities is investigated for both sources. We observe that as the duty cycle of the pulse is decreased the positive ion yield shifted towards higher mass clusters, due to a decrease in gas temperature enabling increased hydration reactions. The negative ions also display similar trends with the yield of larger negative ions increasing with shorter duty cycles. From time-resolved ion intensities it is clearly seen that positive ions are produced in the on-phase of the discharge, and decay in the off-phase. Negative ions, in contrast, are produced mainly in the off-phase of the discharge and decay during the on-phase. With increased distance between source and instrument we observe that the yield of large positive ions increases, at the expense of smaller positive ions which are lost before they reach the orifice. Negative ions, on the other hand, show an increase in yield as distance is increased.

Preliminary analysis of common pharmaceutical products suggest that a decreased duty cycle gives improved identification of negative ion surface compounds however, where surface compounds undergo ionisation to form positive ions, larger duty cycles allowed for better identification. The gas-phase plasma chemistry for different arrangments will be discussed.

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9:40am **AS+BI+IS-WeM6 Comparison of Ambient Pressure Ionization Sources by Determining Useful Yields of Forensic Compounds of Interest**, ***T. Brewer***, *C. Szakal, E. Sisco, S. Muramoto, T. Forbes, G. Gillen*, NIST

The detection of illicit drugs and trace explosives represents one of the most significant challenges for law enforcement and forensic communities. Of particular interest to the forensic analyst is the ability to rapidly identify suspected illicit drug materials and explosives residues in their native state (powder, tablet or liquid form), under atmospheric conditions and with a high level of specificity and sensitivity. To that end there are numerous ambient pressure ionization techniques such as atmospheric pressure glow discharge (APGD), low temperature plasma (LTP), and desorption electrospray ionization (DESI) that can be used to interrogate forensic compounds. However, a method of comparing between the different ambient ionization sources does not exist. Here, useful yields are determined for a series of forensic compounds using different ambient pressure ionization sources as a means of comparison. Using a precision inkjet deposition system a well-defined array of microdrops is produced with each deposit containing a known number of analyte molecules. The individual deposits were removed or desorbed until consumed while monitoring the integrated characteristic molecular secondary ions for each analyte. The ratio of integrated counts to the number of molecules in the deposit defines the useful yield of the experiments. The results here highlight a way to compare the different ambient ionization sources for the analysis of forensic compounds of interest.

10:40am **AS+BI+IS-WeM9 Atmospheric Pressure Ionization Mass Spectrometry: Fundamentals, Simulations, and Applications**, ***Th. Benter***, University of Wuppertal, Germany **INVITED**

Almost for a century now, mass spectrometric instrumentation is generally designed to establish linear analyte concentration – ion signal responses. Deviations from linear relationships are tolerated to a certain extent but such observations usually raises doubts on the performance of the method applied. Surprisingly, Atmospheric Pressure Ionization (API) techniques have swiftly led to the frequent usage of terms such as "matrix effects", "ion suppression", or "non-linear response". This is particularly true for ambient ionization methods. In fact, the various API methods not only target different analyte properties, e.g. gas phase acidities, they also frequently generate new ion signals which are then somehow related to the neutral analyte precursor. On the other hand API mass spectra may also show unexpected fragmentation patterns – despite the often claimed "soft" nature of the ionization processes involved.

In this contribution we are attempting to highlight some of the key processes operating on the primarily generated analyte ion population en route from the origin of ion formation to the collision free analyzer region. For this purpose, we are defining *chemical domains* such as the initial reagent ion generation domain (in ambient ionization often plasmas), the chemical ionization domain, or the thermal ion transport domain, among others. These domains exhibit distinct features, which are significantly changing the chemical matrix in which ions and neutrals are moving towards the collision free - and thus chemically non-reactive - analyzer region.

Primary ionization pathways, subsequent thermal ion molecule chemistry, and electrical fields are discussed as potential drivers of chemical transformation processes, which may render the interpretation of API mass spectra quite difficult. This is particularly true for the analysis of complex mixtures using API MS without chromatographic pre-separation of the neutrals. Ambient ionization methods are generally designed to do exactly that: Analyze samples (e.g., human urine, drug tablets, surface contaminations, to name but a few) without sample preparation and preferentially in real time.

Examples are given to illustrate the extent of selected transformation processes. Among other issues it is discussed why the generation of Helium metastable atoms (He^M) results in protonation in API MS, or why aromatic hydrocarbons ionized with the exact same primary excitation scheme yield almost exclusively radical cations in classical mass spectrometers but often deprotonated molecules in API systems.

11:20am **AS+BI+IS-WeM11 Ambient Mass Spectrometry for Structural Analysis of Organic Monolayers**, ***H. Zuilhof***, Wageningen University, Netherlands

For the analysis of covalently bound organic monolayers a variety of surface-sensitive techniques has been developed, including XPS, AES, IR, contact angle measurements and X-ray reflectivity. While each of these has its own merits, none of them provide **structural** information. In addition, via e.g. XPS it is sometimes possible to follow A -> B reactions on a surface, but A -> x% B + y% C is already nearly impossible to properly analyze. Similar restrictions apply to the study of diluted monolayers (e.g. 10% of a bioactive compound surrounded by 90% inert surface-covering monolayer), while dilution may actually be essential for the proper biological functioning of the monolayer! Therefore novel analysis techniques are still in demand, and here we present the application of DART ambient mass spectrometry as a generic and highly powerful technique for the analysis of such monolayers. Using a variety of tailor-made, covalently attached organic monolayers on silicon nitride and other substrates we show that MS can be used to study: 1) the progress of four sequential surface-bound organic reactions, 2) surfaces with a mixture of halogens on them, 3) the progress of incomplete reactions, and 4) the stability of biofunctional groups. In the current presentation we summarize our recently published work in this area (ChemComm 2013, 922) and present new, as of yet unpublished data that outline the tremendous potential of this novel analysis technique!

11:40am **AS+BI+IS-WeM12 Differentiation of Microbial Species & Strains in Coculture Biofilms by Multivariate Analysis of Laser Desorption Postionization Mass Spectra**, *C. Bhardwaj, Y. Cui,* University of Illinois at Chicago, *H.C. Bernstein, R.P. Carlson,* Montana State University, ***L. Hanley***, University of Illinois at Chicago

The metabolic states of microbial biofilms vary with growth conditions such as host surface, culture media, or antibiotic concentration. 7.87 and 10.5 eV vacuum ultraviolet (VUV) photon energies were used in laser desorption postionization mass spectrometry (LDPI-MS) to analyze microbial biofilms comprised of binary cultures of interacting microorganisms grown on polymer membranes. Principal components analysis (PCA) was applied to the MS data to differentiate species in *Escherichia coli-Saccharomyces cerevisiae* coculture biofilms. PCA of LDPI-MS also differentiated individual *E. coli* strains in a biofilm comprised of two interacting gene deletion strains, even though these strains differed from the wild type K-12 strain by no more than four gene deletions each out of approximately 2000 genes. PCA treatment of 7.87 eV LDPI-MS data separated the *E. coli* strains into two "pure" groups and a distinct mixed region. Furthermore, the "pure" regions of the *E. coli* cocultures showed greater variance by PCA when analyzed by 7.87 eV photon energies than by 10.5 eV radiation. Comparison of the 7.87 and 10.5 eV data is consistent with the expectation that the lower photon energy selects a subset of low ionization energy analytes while 10.5 eV is more inclusive, detecting a wider range of analytes. These two VUV photon energies therefore give different spreads via PCA and their respective use in LDPI-MS constitute an additional experimental parameter to differentiate the metabolite states of microbial biofilms growing on different surfaces.

Biomaterial Interfaces
Room: 201 B - Session BI-WeM

Cell-Surface Interactions
Moderator: M.R. Alexander, University of Nottingham, UK

8:00am **BI-WeM1 High-Throughput Discovery of Materials for Human Pluripotent Stem Cell Culture**, ***A.D. Celiz***, *J.G.W. Smith, A.K. Patel,* University of Nottingham, UK, *R. Langer, D.G. Anderson,* Massachusetts Institute of Technology, *D.A. Barrett, L.E. Young, C. Denning, M.C. Davies, M.R. Alexander*, University of Nottingham, UK

A key hurdle in translating stem cell therapies from research to industrial scale and clinical application is to produce the necessary numbers of cells. For example, a major heart attack causes loss of 1 billion cardiomyocytes and similar cell numbers are lost during progression of other conditions such as multiple sclerosis and diabetes. To meet the demand for such high cell numbers, a defined growth substrate free of animal-derived components is desirable. To this end, we have employed polymer microarrays to screen for human pluripotent stem cell (hPSC) attachment and phenotype on polymers in a high-throughput manner. Polymer microarrays enable a large combinatorial chemical space to be interrogated on a single glass slide. Furthermore, since monomers can be robotically printed and polymerized on the slide via UV photo polymerization, rapid evolution of large numbers of polymers is facilitated. 'Hit' materials identified from the initial screen can be taken forward to a second generation array and mixed in a combinatorial manner to test hypotheses formed from the first generation array and this iteration continues until scaled up to plastic ware for automated culture protocols to achieve long-term expansion of hPSCs.

We have screened over 140 acrylate and acrylamide homopolymers in an array format for hPSC attachment in mouse embryonic fibroblast (MEF) conditioned medium and defined media including StemPro® and mTeSR™1 after 24 hours in culture. Hit materials were then mixed to produce a second generation array of over 500 unique copolymers to optimise cell attachment. Polymer microarrays were characterized using time of flight secondary-ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and water contact angle (WCA) measurements. Multivariate analysis (MVA) was used to successfully predict material wettability and cell performance from the ToF SIMS data. Cell attachment was identified using DAPI (nuclei) staining and maintenance of pluripotency was confirmed by OCT-4 staining and imaged using automated fluorescence microscopy. This approach to materials discovery will provide a defined, synthetic growth substrate for hPSC culture that is amenable to scale up for industrial application and is a step toward xeno-free hPSC culture conditions necessary for clinical application.

8:20am **BI-WeM2 Toxicology of Antimicrobial Conjugated Electrolytes: Interactions with Mammalian Cells**, ***H.E. Canavan***, *K.N. Wilde, D.G. Whitten*, University of New Mexico

Certain cationic phenylene ethynylene (CPE)-based polymers (PPEs) and oligomers (OPEs) exhibit dark- and light-activated antimicrobial activity. Until recently, it was unknown if they would also exhibit similar biocidal activity toward mammalian cells. Based on their biocidal activity and diversity of repeat unit number and functional groups, a variety of CPEs, PPEs, and OPEs were selected for these studies, and were examined for their toxicity toward mammalian cells at three levels: cytoxicity testing of cell monolayers, skin irritation testing of tissues, and intracellular co-localization. As expected, concentration plays the largest role in determining viability. The lack of skin irritation for all substances alleviates initial safety concerns for products based on these CPEs and OPEs. In all

cases, the addition of light changed the effects of the compounds on the mammalian cells. The modes of action of these compounds appear to be governed primarily by length.

8:40am **BI-WeM3** ***In Situ*** **ATR-FTIR of Human Mesenchymal Stem Cell Differentiation**, ***D.E. Barlow****, P.A. Fulmer, T.J. O'Shaughnessy, K.P. Fears, J. Morabito, R. Stine, S.P. Mulvaney, B.R. Ringeisen*, U.S. Naval Research Laboratory

Vibrational spectroscopies are valuable methods for non-destructive characterization of biochemical functionality and physiological changes in stem cells. To date, the primary approaches have almost exclusively used either Raman microscopy or Fourier transform infrared (FTIR) microscopy in transmission or reflection configurations. Another FTIR approach is the interfacially sensitive attenuated total reflectance (ATR) configuration which has often been used for in situ characterization of buried cell-substrate interfaces with live microorganisms such as bacteria. However, so far, the method has rarely been used with mammalian cells. Our approach provides a useful complimentary method for which multiple live specimens can be kept under controlled environmental conditions and analyzed by ATR-FTIR over multi-week periods. As a first step in employing in situ ATR-FTIR, we will present results demonstrating early detection of osteogenic differentiation of live human mesenchymal stem cells (hMSC's). In comparison to control hMSC spectra, hydroxyapetite related bands are clearly observed for cells in osteogenic media within 24 hours. Further hydroxyapetite formation and differentiation characteristics were observed over 2 week periods. Additional results will also be presented comparing interfacial spectra of live hMSC's on surfaces with varying properties, including poly-D-lysine/laminin coated substrates, graphene, and nanocrystaline hydroxyapetite.

9:00am **BI-WeM4 Do Cells Read Braille? High Throughput Screening of Surface Topography-Induced Cellular Responses**, ***J. De Boer***, University of Twente, Netherlands **INVITED**

It is well known that cells can respond to diffusible molecules but it is less well known that they are also able to respond to patterned surface topographies. If we are able to understand how cells respond to these patterns, we can rationally design the surface of medical implants for optimized functionality. To unravel the secret Braille language of cells, we have designed and engineered the TopoChip platform, a library of surface topographies reproduced onto polymeric surfaces. Using high-content imaging, we are able to analyze the response of cells to thousands of different surface patterns simultaneously. Thus, we have found surfaces which induce expression of the early osteoblast marker alkaline phosphatase (ALP) in mesenchymal stromal cells to levels similar to that induced by classical osteoblast inducers such as dexamethasone. In addition to ALP staining, we have also stained the actin cytoskeleton and the nucleus, and using CellProfiler software, we have extracted nearly 300 morphological features for each cell on the TopoChip. Using machine learning algorithms, we are now able to predict ALP expression based on cell morphology alone, and further experiments are in progress to investigate a possible correlation between the actin cytoskeletal organization and ALP expression. In conclusion, using a high-throughput screening approach, we can now start to unravel the secret language of surface topographies and apply the hit surfaces to improve medical implants.

9:40am **BI-WeM6 Less is More: Enhancing the Effect of Fibroblast Growth Factor (FGF2) on Human Dermal Fibroblast Proliferation by Surface Modification**, ***J.D. Whittle***, *D.E. Robinson*, University of South Australia

Often the materials selected for culture-ware, scaffolds or bandages are chosen for their bulk properties and low cost, rather than their suitability for cell culture. Consequently cell culture frequently requires relatively large quantities of expensive growth factors (GFs) and other supplements to be added to the culture medium. Cell response to surfaces is known to be heavily influenced by surface chemistry and topology, which may impact on cell attachment, proliferation or differentiation. These surface properties can affect the growth of cells, they do so by influencing the cellular microenvironment. Often this is by modulating the composition and conformation of adsorbed proteins.

A number of approaches to healing of chronic wounds involve the culture of patient cells on bandages or scaffolds for delivery direct into wounds. In this paper, we describe the approach we have taken in our lab to provide a suitable microenvironment for human dermal fibroblasts.

Inspired by the role of the extra-cellular matrix (ECM) in vivo, we use a plasma polymer surface to bind glycoaminoglycans (GAGs) which are able to capture the growth factor FGF2 from solution. By binding the GAG and growth factor to the culture surface, we achieve significantly higher cell proliferation rates at low serum concentrations than adding these components directly into the culture media. We show that binding GAG and GF to the surface has a cooperative effect, in which the combination of these biomolecules is much more effective than either of them alone. In addition to better performance, the pre-loading of culture surfaces avoids the need to add these reagents to the culture medium and therefore reduces the cost of cell culture. We also show how this approach can be translated from 2d cultures to electrospun scaffolds to provide organised dermal structures of fibroblasts and keratinocytes.

10:40am **BI-WeM9 An Anionic Drug Delivery System using Lecithin Liposomes to Improve Oncolytic Viral Cancer Therapy**, ***N. Mendez***, *V. Herrera, F. Hedjran, S.L. Blair, T. Reid, W.C. Trogler, A.C. Kummel*, University of California San Diego

Several treatment modalities such as surgery, radiation, and chemotherapy are effective for cancer treatment however also face several limitations. Alternatively, oncolytic viruses (OVs) can target multiple mechanisms of action while at the same time exploit validated genetic pathways known to be disregulated in many cancers. In particular, the oncolytic virus TAV-255 has shown viral replication attenuation in normal cells while retaining cytolytic activity in tumor cells by taking advantage of defects in the p53-tumor suppressor pathway. Despite its several advantages, the utility of OVs for cancer therapy is limited by 1) neutralization by antibodies mediated by the immune system, 2) rapid clearance by the reticuloendothelial (RE) system in the liver, and 3) the lack of expression of surface receptors (CAR) in certain cancers necessary for OV transduction. Oncolytic viruses are promising agents to combine with nanoparticle delivery approaches because of the capacity for self-replication of the virus. In systemic delivery, targeting with nanoparticles may focus the viral load to the primary tumor cells as well as metastatic tumors to insure a productive initial infection. A non-toxic liposomal delivery system has been developed for delivery of the virus to tumor cells. Further, with the aim to overcome an immune response and to enhance its potential use to treat primary and metastatic tumors, an encapsulation method involving an anionic non-toxic liposome has been prepared by self-assembly of Lecithin around the viral capsid. The developed method has shown that 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. Extracting non-encapsulated viruses from solution may prevent an adverse immune response when used in an in vivo model and may enhance treatment for multiple administrations.

11:00am **BI-WeM10 Poly(*N*-isopropyl Acrylamide)-coated Surfaces: Investigation of Biocompatibility with Mammalian Cells**, ***M.A. Cooperstein***, *H.E. Canavan*, University of New Mexico

Poly(*N*-isopropyl acrylamide) (pNIPAM) undergoes a conformation change in a physiologically relevant temperature range. PNIPAM is relatively hydrophobic above its lower critical solution temperature (LCST, ~32^{o}C), and mammalian cells are easily cultured on pNIPAM-grafted surfaces. When the temperature is lowered below the LCST, the polymer's chains rapidly hydrate, and cells detach as intact sheets capable of being used to engineer tissues ("cell sheet engineering"). Although the NIPAM monomer is toxic, there are conflicting reports as to whether its polymerized form is toxic, as well. Very few (<10) studies exist that investigate the cytotoxicity of pNIPAM, and their results are conflicting. Furthermore, the published studies are not comprehensive. Before the cell sheets detached from pNIPAM can ultimately be used on humans, it is crucial to first assess the cytotoxicity of the surfaces from which they have been obtained. In this work, we present a comprehensive investigation of the cytotoxicity of pNIPAM-grafted surfaces. The relative biocompatibility of substrates prepared using different polymerization (free radical and plasma polymerization) and deposition (spin coating and plasma polymerization) techniques is evaluated using appropriate cytotoxicity tests (MTS, Live/Dead, plating efficiency). Four different mammalian cell types (endothelial, epithelial, smooth muscle, and fibroblasts) were used for the cytotoxicity testing. The pNIPAM-coated surfaces were evaluated for their thermoresponse and surface chemistry using X-ray photoelectron spectroscopy and goniometry. We find that while cell viability on pNIPAM surfaces decreases when compared to controls, the viability also seems to be deposition type dependent, with sol-gel-based pNIPAM surfaces being the least biocompatible. We attribute this difference to surface topography and chemistry. This work will have valuable insights into the cytotoxicity of pNIPAM-coated surfaces, and therefore into the applicability of cells grown on these surfaces for use in human subjects. In addition, the trends observed in the effect of polymer molecular weight, surface modification technique, and cell type may be extrapolated to other bioactive polymers of interest.

11:20am **BI-WeM11 Polymer Microarrays for the High Throughput Discovery of Novel Switchable Materials**, ***A.L. Hook***, *C. Chang*, University of Nottingham, UK, *R. Langer, D.G. Anderson*, Massachusetts Institute of Technology, *P. Williams, M.C. Davies, M.R. Alexander*, University of Nottingham, UK

Polymer microarrays for the high throughput discovery of novel switchable materials

Andrew L. Hook[a], Chien-Yi Chang[b], Robert Langer[c], Daniel G. Anderson[c], Paul Williams[b], Martyn C. Davies[a], Morgan R. Alexander[a]

[a]Laboratory of Biophysics and Surface Analysis, University of Nottingham, UK

[b]School of Molecular Medical Sciences, University of Nottingham, UK

[c]David H. Koch Institute for Integrative Cancer Research, Massachusetts Institute of Technology, USA

Polymer microarrays have become a key enabling technology for high throughput materials discovery. This format has been applied to a broad range of biological systems, from stem cell attachment to the resistance of bacterial attachment.[1] Switchable materials have also been a focus of materials research as they provide temporal control of biological systems. Switchable materials are able to alter their surface or physical properties in response to an external specific signal such as a change in temperature, pH, or concentration of a signal molecule. This class of materials has been applied to drug delivery and controlled cell attachment.

We have applied polymer microarrays for the discovery of novel switchable materials that are able to temporally manipulate biological systems.[2,3] Polymer microarrays were formed by printing mixtures of acrylate monomers, followed by UV curing and vacuum extraction. This enabled arrays of hundreds of unique materials to be produced. We screened these materials for switchable properties using AFM, WCA, optical microscopy and ToF-SIMS. The focus of this work was to identify materials with thermally induced changes in chemistry or topography.[2,3] Using these methods we discovered novel materials with unique switchable properties. In particular, ToF-SIMS analysis provided insight into the conformational changes induced in the polymers by the change in temperature.[2] These were applied to investigate the attachment of bacteria to surfaces, where we were able to temporally control the interaction of bacteria with a polymer surface. These materials have potential application for regenerative filtration devices.

1. Hook et al., *Biomaterials*, **2010**, 31, (2), 187-198.

2. Hook et al., *Surface and Interface Analysis*, **2013**, 45, (1), 181-184.

3. Hook et al., *Soft Matter*, **2011**, 7, (16), 7194-7197.

11:40am **BI-WeM12 Antibacterial and Cells Proliferation Studies of Biodegradable Polymeric 3D Scaffolds**, ***A. Pegalajar-Jurado***, *K.A. Wold, M.M. Reynolds, E.R. Fisher*, Colorado State University

Wounds caused by diseases or injuries often present complications, requiring medical intervention to restore biochemical processes needed for proper healing to occur. Several biodegradable polymeric materials have been applied to wounds for protection and to facilitate the healing. These materials, however, often do not inhibit bacterial infection nor support cell growth.

Development of therapeutic materials that release antimicrobial agent from a porous, polymeric fibers scaffold has been previously reported by our group, which was directly related to the release of nitric oxide (NO). These scaffolds showed a release of NO under physiological pH and temperature, and a log2 reduction in *Acinetobacter baumannii* was achieved using 15 mg/mL of NO releasing S-nitrosated poly(lactic-*co*-glycolic-*co*-hydroxymethyl propionic acid (PLGH)-cysteamine. However, fibroblast cells showed low viability when exposed to concentrations higher than 0.1 mg/mL of S-nitrated PLGH-cysteamine polymer. A log5 reduction in bacteria such as *Escherichia coli* and methicillin-resistant *Staphylococcus aureus* is required to be considered medically relevant. To achieve this goal, a multiple therapeutic strategy was implemented. The antimicrobial activity of silver nanoparticles against *E.coli* and *S.*aureus over short period of time is well established. To obtain a long term efficacy as well as local toxicity, silver nanoparticles were incorporated within the NO releasing scaffolds. This combination is expected to result in antibacterial activity against multiple strains included *E.coli* and MRSA.

Plasma processing has been used extensively to modify two-dimensional materials. Recently, however, plasma treatments have been used to successfully modify three-dimensional (3D) structures. Our preliminary data demonstrate that porous (Ɛ-caprolactone) (PCL) scaffolds can be modified by plasma functionalization. Significant increase in the scaffolds' wettability was achieved by H_2O/NH_3 and H_2O/N_2 plasma treatments. XPS analysis corroborated changes in the surface chemistry throughout the 3D structure, with no significant changes in scaffold morphology after plasma treatments (SEM analysis). In addition, enhanced osteoblast proliferation was observed in PCL scaffolds after plasma surface modification. These results support plasma surface modification as a viable technique to improve the surface properties of 3D materials to promote cell growth and ultimately aid in tissue engineering. In addition to these results, cell proliferation and the antimicrobial behavior of S-nitrated PLGH-cysteamine polymer after the incorporation of silver nanoparticles and plasma surface modification will be discussed.

Nanometer-scale Science and Technology
Room: 203 B - Session NS+AS+BI+SP-WeM

Nanoscale Imaging and Microscopy
Moderator: U.D. Schwarz, Yale University

8:00am **NS+AS+BI+SP-WeM1 Outcomes of and Materials for Two University-Level Courses on Atomic Force Microscopy**, ***N.A. Burnham***, Worcester Polytechnic Institute

The outcomes of and materials for undergraduate and graduate courses on atomic force microscopy (AFM) in the Physics Department at Worcester Polytechnic Institute are described [1]. Given since 2001, the courses have been well received by over 150 students – from freshmen to emeritus professors – 45% of whom go on to use their AFM skills in subsequent studies or professions. Over half of the enrollees have been students external to the author's home department. The course materials that have been developed are: YouTube videos [2], instrument lab instructions, computer lab instructions and programs, instructions and programs for labs with a macroscopically sized cantilever, classroom materials including writing exercises, and notes for teaching assistants and lecturers. Still under development is a textbook with homework problems. Most materials are available upon request from the author in order to promote AFM courses at other institutions, with the intent to draw more students into the intriguing world of nanoscience.

1. Accepted for publication in J. Nano Education

2. http://www.youtube.com/user/AtomicForceMicro/featured

8:20am **NS+AS+BI+SP-WeM2 Imaging Li and B in a Glass Sample with 100nm Lateral Resolution Using NanoSIMS**, ***Z. Zhu***, Pacific Northwest National Laboratory, *Y. Wang*, University of Florida, *J. Crum*, Pacific Northwest National Laboratory, *Z. Wang*, Chinese Academy of Science

A widely used method to immobilize nuclear wastes is fusing them into glasses. These proposed glass waste forms are multicomponent complex material with the common components of Li and B compounds. During the fast cooling process, phase separation occurs in the form of 200-500 nm clusters and the glass matrix. It is difficult for commonly-used surface analysis tools (e.g., X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy, scanning electron microscope/energy dispersive spectroscopy (SEM/EDX), and transmission electron microscope/energy dispersive spectroscopy (TEM/EDX)) to characterize the distributions of ultra-light elements like Li and B in these two phases. For example, although TEM/EDX characterization can show mapping of heavy elements in the two phases, this technique is not ideal to identify the location of ultra-light elements, such as Li and B, because the sensitivity of EDX analysis for Li and B is poor. NanoSIMS can provide nano-scale spatial resolution (down to 50 nm) as well as excellent sensitivity for Li and B, making it a good candidate to image Li and B in the glass sample. We have used NanoSIMS to map Li and B in the glass sample with a lateral resolution of ≤ 100 nm. NanoSIMS images clearly show enrichment of both Li and B in the matrix phase.

8:40am **NS+AS+BI+SP-WeM3 Visualization of Subsurface Features in Soft Matrix using Atomic Force Microscopy Techniques**, ***K. Kimura***, *K. Kobayashi, H. Yamada*, Kyoto University, Japan

Imaging of deeply buried subsurface features in soft matrices such as parasites in red blood cells [1], carbon nanoparticles in living cells [2], and buried electronic circuit in industrial products [3] have been demonstrated by heterodyne force microscopy [4] (HFM). Subsurface imaging using ultrasonic AFM (UAFM), which is a technique to evaluate contact stiffness with high sensitivity, has also been demonstrated in some papers. However, UAFM has been mainly applied for imaging subsurface features in hard matrices such as Si and metals, whose resolved maximum depth was typically less than 200 nm [5]. In this study, we visualized Au nanoparticles buried in a polymer matrix under 960 nm from the surface by using HFM and UAFM, which has never been achieved [6].

A dispersion of Au particles (50-nm-diameter) was dropped on a polyimide sheet (125-micro-meter-thick). After drying, a top-coat (photo polymer)

was spin-coated on it and annealed at 150°C. Top-coat thickness was estimated from the film coated on a Si wafer. We used a modified commercial AFM instrument (JEOL: JSPM 4200). The sample was directly glued on a piezoelectric plate, which was fixed on a tube scanner. Another piezoelectric plate for HFM was attached on a cantilever holder. The contact resonance frequency used for imaging was determined by measuring the thermal noise spectrum of the cantilever contacted on the sample. The schematic diagrams of HFM and UAFM are shown in Figs. 1 and 2 in the supplemental file.

We performed subsurface imaging for the samples with the top-coat thickness of up to 1 micro-meter. We found that the maximum depth of the subsurface features resolved by HFM and UAFM depends on the spring constant (*k*) of the cantilever. Figure 3 in the supplemental file shows subsurface images of Au particles buried under a top-coat of 900-nm-thick obtained by UAFM using a Si cantilever (k: 1.3 N/m), which we found the most suitable for subsurface imaging on the polymer matrix. We suppose that subsurface features in a soft matrix at least buried under 1 micro-meter from the surface affect surface viscoelasticity, which are detected by AFM techniques when a cantilever of suitable stiffness is used.

This work was supported by the Murata Science Foundation and Grant-in-Aids from the Japan Society for the Promotion of Science (JSPS).

[1] G. S. Shekhawat et al., Science **310** (2005) 89.

[2] L. Tetard et al., Nature Nanotech. **3** (2008) 501.

[3] S. Hu et al., J. Appl. Phys. **109** (2011) 084324.

[4] M. T. Cuberes et al., J. Phys. D **33** (2000) 2347.

[5] Z. Parlak et al., J. Appl. Phys. **103** (2008) 114910.

[6] K. Kimura et al., Ultramicroscopy (2013) in press (10.1016/j.ultramic.2013.04.003).

9:00am **NS+AS+BI+SP-WeM4 Nanoscale Characterization Using Resonance Enhanced Infrared Spectroscopy**, ***E. Dillon***, *M. Lo, C. Prater, K. Kjoller,* Anasys Instruments, *M. Belkin, F. Lu*, University of Texas at Austin

As current research focuses on shrinking the size of devices and the components that comprise these devices, the characterization of these systems becomes more and more challenging. The resolution of conventional IR spectroscopy techniques is diffraction limited to a practical resolution limit of ~ 3 μm. This length scale is too large to observe any potential nanoscale features on today's devices. Atomic force microscopy (AFM) is a widely used nanoscale imaging technique that provides the user with a high spatial resolution topographic map of a sample surface. When combined; the resulting AFM-IR can provide the high resolution topographic maps commonly associated with AFM with the addition of high spatial resolution IR spectroscopy and IR imaging. Currently, AFM-IR spectroscopy has the ability to collect IR spectroscopic information below the diffraction limit with a lateral resolution of ~ 100 nm. However, there are still some limitations that prevent its use on many important nanoscale systems. One of the main limitations is the thickness of sample required for examination (> 100 nm). Overcoming these limitations has a dramatic impact by enabling widespread use of nanoscale IR spectroscopy for spatially resolved chemical characterization. The use of a quantum cascade laser (QCL) as the IR source significantly increases the sensitivity of AFM-IR. The QCL has repetition rates 1000 times higher than previous lasers used for AFM-IR. This allows the ability to pulse the laser at the resonant frequency of the AFM cantilever giving rise to a high IR sensitivity mode referred to as resonance enhanced infrared nanospectroscopy (REINS). Due to the increased IR sensitivity, less laser power is required to generate a spectrum, meaning samples that were too thin or easily damaged using previous AFM-IR techniques can now be easily examined. Using REINS we have been able to collect nanoscale IR spectra and perform chemical imaging on films as thin as 10 nm. These advances in AFM-IR allow for the characterization of samples from a wide variety of applications, including, organic photovoltaic materials, materials for energy generation and storage, cellular biology, development of advanced polymeric materials and integrated circuit devices.

9:20am **NS+AS+BI+SP-WeM5 AFM-based Chemical and Mechanical Property Characterization of Low-k/Cu Interconnects**, ***M. Lo***, Anasys Instruments, *S.W. King,* Intel Corporation, *E. Dillon, Q. Hu, R. Shetty, C. Prater*, Anasys Instruments

Infrared (IR) spectroscopy is a powerful technique for characterizing the chemical bonding in low dielectric constant (i.e. low-k) materials utilized in nano-electronic Cu interconnect structures. Combined with nanoindentation and other techniques, IR spectroscopy has enabled the structure-property relationships in these materials to be determined. However, such property analysis have been primarily limited to characterizing blanket films due to the spatial resolution of a typical IR measurements being diffraction limited to ca. 3 - 10 μm. Further advances in low-k materials and failure analysis would be greatly enhanced by the ability to perform IR spectroscopy and other material property characterization on actual nanometer scale low-k/Cu interconnects. In this report, we demonstrate both AFM based IR chemical analysis and contact resonance mechanical analysis of a single layer 90 nm low-k/Cu interconnect structure.

To achieve better spatial resolution in IR spectroscopy measurements, a broadly tunable infrared laser was coupled to an atomic force microscope (AFM-IR). IR laser pulses at the wavelengths of the low-k materials characteristics absorption bands was utilized to create rapid thermal expansion that invoked vibrations in the AFM tip directly in contact with the sample. Amplitudes of the ringing motion of the AFM tip were recorded as the same tip scanned over the areas of interest. By detecting only the perturbations directly underneath the AFM tip, spatial resolution below the diffraction limits of IR radiation could therefore be achieved. In this manner, IR spectra and 2D images of a < 1.5 μm wide interlayer dielectric (ILD) in a low-k/Cu interconnect were achieved.

To complement the AFM-IR technique and achieve nanometer scale structure property measurements, AFM-based contact resonance (CR-AFM) measurements were performed in parallel. The CR-AFM technique probes the relative mechanical property of different materials and has been previously demonstrated useful for characterizing the elastic properties of low-k material in similar Cu interconnect structures. For the current CR-AFM measurements, the resonant frequency of the AFM tip was controlled by modulating the alternating current going through a specialized ThermaLever™, which interacts with the magnetic field of a magnet nearby. As this tip scans from ILD to other metallic layers, the frequency of the AFM tip vibration changes due to the variations in the mechanical stiffness from one material to another. By combining the AFM-IR and CR-AFM techniques, both chemical and mechanical analysis of a low-k/Cu nano-electronic structure were achieved using an AFM at high spatial resolution.

9:40am **NS+AS+BI+SP-WeM6 Amino Acid Immobilization and Surface Diffusion of Copper**, *E. Iski,* University of Tulsa, ***A.J. Mannix***, *B.T. Kiraly, M.C. Hersam,* Northwestern University, *N.P. Guisinger*, Argonne National Laboratory

The 2D-scale study of relevant biomolecules, like amino acids, is pertinent for a variety of applications from the origin of biological homochirality and the amplification of surface chirality to the examination of noncovalent supramolecular interactions. Importantly, the study of these molecules on a copper surface may also be significant to the medical community as the binding of amino acids/proteins to copper ions plays a major role in the development of neurodegenerative diseases, like Mad Cow's Disease and Alzheimer's. The need for pristine molecular resolution of these systems requires the use of ultra-high vacuum scanning tunneling microscopy (UHV STM) as the primary technique for these studies. Through the detailed examination of the self-assembly behavior of five amino acid molecules on a Cu(111) single crystal, a fascinating and unexpected phenomenon was discovered. All of the amino acids assisted in the immobilization of copper atoms on the surface. The energetic landscape of the surface as mediated by temperature and molecular coverage facilitated the growth of copper islands and clusters. The growth and size fluctuation of the islands offered an interesting snapshot of metal nanocluster diffusion that often occurs at time scales beyond the resolution of a given surface science technique. The presence of ~1 ML of molecules on the surface effectively trapped the metal atoms into localized islands. Elevated temperatures (≤ 350 K) were used to promote further diffusion, coalescence, and extinction of the islands for a more detailed understanding of the coarsening and ripening mechanisms. In conclusion, while these systems provide insights into the chiral assembly of amino acids on Cu(111), they also provide a unique glimpse into metal surface diffusion and offer the ability to study the mass transport of metal atoms, which is important for the understanding of thin film growth and its morphological evolution.

10:40am **NS+AS+BI+SP-WeM9 Catalytic Model Systems Studied by High-Resolution, Video-Rate Scanning Tunneling Microscopy**, *F. Besenbacher,* Aarhus University, Denmark, ***J. Kibsgaard***, Stanford University **INVITED**

For decades single-crystal surfaces have been studied under ultra-high vacuum (UHV) conditions as model systems for elementary surface processes. This "surface science approach" has contributed substantially to our understanding of the processes involved in especially catalysis.

In this talk I will show how STM can reveal fundamental processes in relation to catalysis, and how we can extract quantitative information on surface diffusion of adatoms and molecules. We use time-resolved, high-resolution STM images/movies to understand diffusion of vacancies, interstitials and molecules, e.g. water molecules on oxide surfaces, sintering and diffusion of nanoclusters on oxide surfaces, diffusion of intermediate species, and to identify active sites and to determine new nanostructures

with novel catalytic properties (see www.phys.au.dk/spm). The atomic-scale information obtained may even lead to the design of new and improved catalysts in certain cases.

11:20am **NS+AS+BI+SP-WeM11 Scanned Probe Based Nanofabrication on Silicon: Progress, Challenges and Technology Spin-Offs**, ***J.W. Lyding****, University of Illinois at Urbana Champaign **INVITED**
Atomic-scale nanofabrication on Si(100) surfaces can be achieved by using hydrogen as an atomic layer electron resist. Electrons from a STM probe can create atomically precise patterns of clean silicon under ultrahigh vacuum conditions. These patterns can serve as templates for selective chemistry, including the atomically precise placement of molecules on the silicon surface. By performing these studies under UHV conditions it is also possible to obtain information about the hydrogen desorption process. Two desorption regimes are observed. The first involves the direct excitation of the bonding-to-antibonding transition and requires an electron energy of ~6.5 eV. In this regime a constant quantum desorption efficiency is observed irrespective of the electron current. At electron energies insufficient to excite the direct bonding-to-antibonding transition, desorption also occurs but with a strong current-dependent desorption efficiency. In this regime, the STM electrons inelastically excite the Si-H vibrational modes, which have a long lifetime of ~10 ns. Thus, if the excitation rate, which depends on the electron current, exceeds the quenching rate by the lattice, then the Si-H bond moves up its vibrational state ladder until desorption occurs from the hot ground state. Atomic resolution patterning is a side benefit of this vibrational heating process since tunneling electron energies are involved. Following a suggestion by Avouris, these experiments were extended to deuterated Si(100) surfaces where a giant kinetic isotope effect was observed. In the single-particle desorption regime, when excitation to the antibonding level occurs deuterium accelerates more slowly away from the silicon surface, thereby enhancing the probability that the bond will reform. Experimentally, deuterium is observed to be about two orders of magnitude more difficult to desorb than hydrogen. In the vibrational heating regime the deuterium desorption probability decreases by many orders of magnitude due to the short Si-D vibrational lifetime (< 1 ns). The STM isotope experiments set the stage for the discovery that deuterium can be used to dramatically reduce hot carrier degradation in silicon CMOS technology. Hot carriers at the transistor gate dielectric-silicon interface desorb the hydrogen used to passivate silicon dangling bonds. Deuterating the interface increases chip hot carrier lifetimes by more than an order of magnitude. Consequently, deuterium processing is now used in advanced chip manufacture. We have also developed a novel tip sharpening method for STM and AFM probes that results in sub-5 nm radii probe tips with ultra-hard conductive coatings.

*** NSTD Recognition Award**

Biomaterial Interfaces
Room: 201 B - Session BI+AI+AS+BA+IA+NL+NS+SP-WeA

Characterization of Biointerfaces
Moderator: A. Rosenhahn, Ruhr-University Bochum, Germany

2:00pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA1 Barrier Properties of the Three Layers of the Stratum Corneum to Metal Ions Analyzed by TOF-SIMS**, *I. Ishizaki*, ULVAC-PHI, Inc., Japan, ***J.S. Hammond***, Physical Electronics Inc., *A. Kubo, H. Kawasaki, K. Nagao*, Keio University, Japan, *Y. Ohashi*, ULVAC-PHI, Inc., Japan, *M. Amagai, A. Kubo*, Keio University, Japan

The stratum corneum (SC) is the outermost barrier protecting the mammalian body from desiccation and foreign insults. Congenital SC barrier insufficiencies, i.e., filaggrin deficiency, are hypothesized to predispose patients to atopic diseases. The insoluble nature of the SC has hampered in-depth-analysis of its barrier function by conventional cell biological methods. Here, we applied time-of-flight secondary-ion-mass-spectrometry (TOF-SIMS) imaging technology to analyze the SC in skin sections of wild type and filaggrin knockout mice.

TOF-SIMS enabled the visualization of the distribution of natural substances and the infiltration of externally applied molecules directly without any staining procedure. The distribution of potassium (K) and arginine revealed that the SC consists of three sharply demarcated layers. K was concentrated in the upper layer, while arginine, a major component of the filaggrin-derived natural moisturizing factors, was specifically concentrated in the middle layer and markedly decreased in the filaggrin knockout SC. When skin was soaked in water, K of the upper layer disappeared. When the mice tails were soaked in solutions of K or hexavalent chromium before cross-sectioning, the TOF-SIMS line scan data indicates that the upper layer of the SC allowed the influx of these ions, suggesting that this layer acts like a "sponge" allowing the passive influx and efflux of exogenous ions. The middle layer blocked the influx of K and hexavalent chromium ions, but failed to block the influx of trivalent chromium ions, which was blocked at the lower layer. Therefore the middle and lower layers have distinct barrier properties depending on each metal. Filaggrin deficiency resulted in the abrogation of the lower layer barrier, allowing trivalent chromium to permeate through the SC to viable epidermal layers. These results, obtained by TOF-SIMS analyses, reveal that the SC consists of three layers of distinct functional properties and demonstrate the loss of barrier properties for particular metal ions in filaggrin deficient SC samples.

2:20pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA2 Imaging Hydrated *Schewanella p.* Biofilm in a Microfluidic Reactor by ToF-SIMS**, ***X.Y. Yu***, *M. Marshall, B. Liu, Z. Zhu, L. Yang, E. Hill, S. Belchik*, Pacific Northwest National Laboratory

We recently developed a microfluidic interface that enables direct probing of liquid surface in vacuum using ToF-SIMS and SEM. The device contains a 100 nm thick silicon nitride (SiN) membrane as the detection area (1.5 ´ 1.5 mm^2) and the microchannels fabricated from polydimethylsiloxane (PDMS) using soft lithography. The unique aspect of our approach is that the detection window is an aperture of 2-3 m m diameter, which allows direct detection of the liquid surface and use surface tension to hold the liquid within the aperture. Its application in ToF-SIMS as an analytical tool was evaluated. In this paper, we present new results of using the microfluidic flow cell to grow *Schewanella p.* biofilm and characterize the biofilm subsequently using ToF-SIMS in the hydrated environment. Depth profiling was used to drill through the SiN membrane and the biofilm grown on the substrate. A controlled media sample was used to compare with the wet biofilm sample. In addition, dry samples deposited on clean silicon wafer were studied to show the difference between wet and dry samples. Multivariate statistical analysis including Principle Component Analysis was used to investigate observations. Our results indicate that imaging biofilm in the hydrated environment using ToF-SIMS is possible using the unique microfluidic device for the first time. Moreover, characteristic biofilm fragments were observed in the wet sample than in dry sample, illustrating the advantage of imaging biofilm in the hydrated state.

2:40pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA3 High-resolution Secondary Ion Mass Spectrometry Imaging of Distinct Lipid Species in the Plasma Membranes of Mammalian Cells**, ***M.L. Kraft***, University of Illinois at Urbana Champaign **INVITED**

The plasma membrane is the selectively permeable lipid bilayer that separates every cell from its surroundings. In mammalian cells, the plasma membrane contains domains of differing protein composition. Growing evidence suggests that each different lipid species and cholesterol are also organized into compositionally and functionally domains within the plasma membrane. Domains that are enriched with cholesterol and sphingolipids, which are often referred to as lipid rafts, are hypothesized to be present in the plasma membrane and influence its functions. Despite this potential importance, the organizations of cholesterol and sphingolipids in cell membranes are poorly understood. Until recently, the distributions of most lipid species could not be directly imaged without the use of fluorophore labels, which may alter the distributions of the lipid molecules that they label. We have combined high-resolution SIMS, which is performed with a Cameca NanoSIMS 50, with metabolic stable isotope labeling in order to visualize the organizations of rare isotope-labeled lipids in the plasma membrane by mapping their distinctive isotope enrichments. Here, the details of this approach and its application to imaging the distributions of metabolically incorporated ^{15}N-sphingolipids and ^{18}O-cholesterol in the plasma membranes of fibroblast cells will be presented. Use of this approach to evaluate hypotheses concerning the mechanisms that regulate lipid organization within the plasma membrane will also be discussed.

4:00pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA7 Analysis of Breast Cancer Tumors with ToF-SIMS**, ***L.J. Gamble***, *M. Robinson*, University of Washington, *F. Morrish, D. Hockenbery*, Fred Hutchinson Cancer Research Center

Tumor metabolism plays a large role in cancer onset and progression, and its causes and effects are under intense scrutiny. Recently, the lipid metabolism in tumors has been looked at as a factor in tumor type and treatment. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is well suited for analysis of the lipid distribution in tumors. In this study, frozen breast cancer tissue specimens from patients were cut using a cryomicrotome at a thickness of 4µm and deposited on silicon wafers. Serial tissue slices were stained with hematoxylin and eosin (H&E) and were used to determine from which structures the various chemical signatures originated. SIMS tissue sample data were acquired on an IONTOF TOF.SIMS V using Bi_3^+ in both high mass and high spatial resolution modes on both ER+ and ER- human breast tumor tissue samples. Mass fragments spectra from multiple spots and tissue slices for the ER+ and ER- tissue samples can be separated from one another using PCA within a 95% confidence interval. Key differences between tissue types are abundance of cholesterol and triacylglycerides/diacylglycerides (TAGs/DAGs). Imaging ToF-SIMS of theses samples show variances for different fatty acids (saturated versus unsaturated) that correlate with model studies using similar cancer cell types.

4:20pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA8 Tools For TOF-SIMS Image Analysis**, ***D.J. Graham***, *L.J. Gamble, D.G. Castner*, University of Washington

The use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) for imaging has increased in recent years. This is due to the improvements in spatial resolution and ion yields from modern primary ion sources. These improvements have made ToF-SIMS attractive for cell and tissue imaging, especially due to the fact that ToF-SIMS can detect and identify a wide range of membrane lipids and other cellular components, and can potentially image these in both 2D and 3D. Characterization of tissues and cells by ToF-SIMS often requires advanced data collection and analysis methodologies including the use of stage rastering for large area analysis and 3D depth profiling. It is also often of interested to localize specific areas within a cell or tissue and carry out region of interest (ROI) analysis. Finally, ToF-SIMS image analysis presents challenges due to the shear size of the data sets. In order to deal with these large, complex data sets, we have created a set of Matlab toolboxes for multivariate analysis of both images and spectra. This talk will highlight new tools in the NBtoolbox that enable the user to process stage raster images, overlay images, and extract ROI images based off of image masks created from any imported image.

For example, the stage raster tools enable the user to import and run PCA on an entire stage raster image, or to dice the stage raster into separate image tiles that can then be analyzed individually. The ROI generation tools enable the user to import any image to be used as a ROI mask. Examples will be shown using florescent images from confocal microscopy as masks to extract ROI from ToF-SIMS images of mouse muscle tissue. Tools are

also included for image alignment, and image cropping. All data processed with these tools can be analyzed using PCA, MAF or MCR.

4:40pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA9 How Hydration Affects Mechanical Anisotropy, Nano-Topography and Fibril Organization of Osteonal Lamellae**, *A. Faingold*, ***S.R. Cohen***, Weizmann Institute of Science, Israel, *R. Shahar*, Koret School of Veterinary Medicine, The Hebrew University of Jerusalem, *S. Weiner, H.D. Wagner*, Weizmann Institute of Science, Israel

Water serves a central role in physiological systems. Even bone, a relatively "dry" component, has high water content: cortical (also known as compact) bone contains about 20% water by volume. The water content varies with age, and influences the structural and mechanical properties of the bone, from the level of mineralized fibrils up to osteonal lamellae. Many studies on mechanical properties of bone are performed on bone which has been dehydrated to some degree, whereas the relevant physiological state is wet. In this work, atomic force microscopy, nanoindentation, and microindentation have been applied to wet and dry bone samples in order to investigate the influence of hydration at different hierarchical levels; the mineralized fibril level (~100nm), the lamellar level (~6µm); and the osteon level (up to ~30µm). Measurements were made both in directions parallel and perpendicular to the osteonal axis by cutting appropriate slices from a metacarpal bone of a 5 year old male horse. "Dry" samples were obtained by allowing the polished sample to stand under ambient conditions for 24 hours. "Wet" samples were measured under deionized water, or PBS solution in which they were incubated between 1 - 18 hours prior to measurement. We note that under these conditions, the wet samples contained 12% water whereas dry samples contained 9% water. Nonetheless, significant differences between the two states were observed: (1) Dry samples were both stiffer and harder than the wet samples in both directions studied, and at all length scales. (2) The anisotropy ratio, ratio of modulus or hardness along vs. perpendicular to the osteonal axis, was larger in the dry samples than for the wet ones. (3) These mechanical changes are accompanied by marked variation in the sample topography as observed by atomic force microscopy. These results will be presented in the context of related work. A model we developed based on differences in the fibril orientation between dry and wet states provides a good rationale for the observed behavior.

5:00pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA10 AFM of Supported Lipid Bilayers: From Critical Point Behaviour to Actin Polymerization**, ***G.R. Heath***, *S.D. Connell, S.D. Evans*, University of Leeds, UK

In this study we create supported lipid model membranes which display phase separation into liquid-ordered and liquid disordered domains and use atomic force microscopy (AFM) to observe critical phenomena and protein interactions with the aid of stable and precise temperature control. The regions of criticality were determined by accurately measuring and calculating phase diagrams for the 2 phase L d –L o region, and tracking how it moves with temperature, then increasing the sampling density around the estimated critical regions. Compositional fluctuations were observed above the critical temperature (T c) and characterized using a spatial correlation function. From this analysis, the phase transition was found to be most closely described by the 2D Ising model, showing it is a critical transition. The region of critically fluctuating 10–100 nm nanodomains has been found to extend a considerable distance above T c to temperatures within the biological range, and seem to be an ideal candidate for the actual structure of lipid rafts in cell membranes. Although evidence for this idea has recently emerged, this is the first direct evidence for nanoscale domains in the critical region.

Ponticulin is a 17KDa integral membrane protein with multiple membrane spanning beta strands and glycosylphosphatidylinositol (GPI) lipid anchor at its C-terminus. Ponticulin has been shown to be the major high affinity link between the plasma membrane and the cortial actin network in *D. discoideum* (Wuestehube and luna, 1987; Chia et al., 1991). This protien in thought to reside in cholesterol-rich lipid microdomains ('lipid rafts') with the transmembrane domain apparently lying outside the lipid raft with the raft localization being dependant upon the GPI anchor at the C-terminus of the protein. We test the hypothesis of localization and show for the first signs of GPI-anchored membranes proteins preferentially locating to boundaries between the lo and ld phase. This may provide a potential mechanism by which the cytoskeleton can influence lipid organization.

Cationic lipids have been previously shown to adsorb actin from a non polymerizing solution, induce its polymerization, and form a 2D network of actin filaments, in conditions that forbid bulk polymerization. We show this phenomenon on supported lipid bilayers using high resolution AFM and QCM-D, investigating various factors such pH, charge concentration and lipid mobility which affect the actin structures formed. We then go on to mathematically model this process to show 2 different polymerization mechanisms depending on the lipid diffusion.

5:20pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA11 Investigating Reversible Dye Adsorption on TiO_2: A QCM-D Study**, ***H.K. Wayment-Steele***, *L.E. Johnson*, Pomona College, *M.P. Dixon*, Biolin Scientific, *M.S. Johal*, Pomona College

Understanding the kinetics of dye adsorption on semiconductors is crucial for designing dye-sensitized solar cells (DSSCs) with enhanced efficiency. Harms et al. (2012) have recently demonstrated the applications of QCM-D to show in-situ dye adsorption on flat TiO2 surfaces. QCM-D provides adsorption measurements in real time and therefore determination of the kinetics of the process. In this work, we examine reversible, non-covalent binding of N3, a commercial RuBipy dye, using the native oxide layer of a titanium sensor to simulate the TiO_2 substrate of a DSSC. To isolate the weak binding mode, we deactivated the carboxylate groups of N3 by forming methyl esters, thus disabling chelation to TiO_2. Improved understanding of the weak binding mode provides insight into dye aggregation and the relative contributions of chelation versus non-covalent processes.

5:40pm **BI+AI+AS+BA+IA+NL+NS+SP-WeA12 Combined Raman Systems for Biological Imaging and Analysis**, *A.J. King*, Renishaw Inc, *T. Prusnick*, Renishaw Inc., ***M. Canales***, Renishaw Inc

Raman microscopy has become a routine tool for many materials, but the need for this molecular imaging and analysis technique in biological research has become essential. The ability probe the chemical and molecular structure of biological materials is obtained directly without the need for any dyes or markers. These systems can be utilised to generate chemical images of cells, tissue, bone and bio-compatible materials with very high spatial resolution. It has been employed for cancer diagnosis, stem cell differentiation, skin treatments, protein structure analysis, bio-diagnostics, bacterial identification and green energy.

This Raman instrumentation can also be combined with environmental chambers, scanning probe techniques, scanning electron microscopes and in-vivo probes; to provide in-situ and co-localised measurements. This talk will provide an introduction to Raman microscopy with biological materials; the instrumentation required for these techniques; and, will highlight some applications where Raman microscopy is making the biggest impact with biological materials.

Nanometer-scale Science and Technology
Room: 203 B - Session NS+BI+EM-WeA

Nanopatterning and Nanolithography
Moderator: P.E. Sheehan, Naval Research Laboratory

2:20pm **NS+BI+EM-WeA2 Tunneling Electron Induced Adsorption of Copper Phthalocyanine on the Cu(111) Surface**, ***T. Stock****, *J. Nogami*, University of Toronto, Canada

The adsorption of up to one monolayer (ML) of copper phthalocyanine (CuPc) molecules on a room temperature Cu(111) surface has been studied using scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Below 1 ML the molecules are in a fluid state and are highly mobile on the surface. At 1 ML coverage the molecules coalesce into a highly ordered 2D crystal phase. At sub-ML coverages, adsorption of individual CuPc molecules can be induced through exposure to tunneling electrons at a bias voltage exceeding a threshold value . This tunneling electron induced adsorption effect allows for a novel variety of molecular STM lithography, and permits probing of the mechanisms involved in the adsorption of individual molecules.

2:40pm **NS+BI+EM-WeA3 STM Study of Pyramid Structures on Ge(110) Formed by Argon Ion Sputtering**, *M.S. van Zijll, S. MacIntyre,* ***S. Chiang***, University of California, Davis

Defects often act as nucleation points for island growth on surfaces. Earlier studies found that sputtering surfaces of silicon and germanium could create ordered arrays of dot and ripple structures. As a result of the sputtering and annealing cleaning procedures on Ge(110), we had previously observed the formation of pyramid structures, which could serve as engineered defects for island growth. Although these structures had some similarities to the dot patterns observed by other groups, the better defined shapes and the larger separation between the pyramid structures were striking. In an effort to better understand and control the formation of these defects, we used scanning tunneling microscopy (STM) under ultra high vacuum (UHV) conditions to measure the shapes, sizes, and spatial distribution of the observed pyramid structures on Ge(110) as a function of the argon ion

*** NSTD Student Award Finalist**

sputtering energy. The samples were sputtered with low-energy ions ranging from 200eV to 500eV at an incident angle of 34°. The bases of the pyramids are rhombuses due to the 16x2 reconstruction of the Ge(110) surface. The lengths of the rhombuses range from 10 to 80nm, and the side-walls slant upward at ~4° from the horizontal. A Monte Carlo simulation of the sputtering process is used to determine the dependence of the sputtering yield on the binding energy of the surface atoms and on the incident ion energy, thereby giving insight into the process of pyramid formation.

3:00pm **NS+BI+EM-WeA4 Enhanced Electrical Conductivity by Au Nanoparticle Islands Deposited from Solution**, ***F. Jiang***, *A.J. Muscat*, University of Arizona

Colloidal Au nanoparticles (NPs) capped with tetraoctylammonium bromide (TOAB) were synthesized using the Brust method, and deposited on oxidized p-type Si(100) covered by either 3-aminopropyltrimethoxysilane (APTMS) or 3-mercaptopropyltrimethoxysilane (MPTMS). Dip coating was used to deposit the Au NPs with nominal diameters of 5-20 nm using the linker 1,2-ethanedithiol (EDT). One coating cycle consisted of immersion in the Au NP colloid for 1 h, rinsing in toluene, immersion in EDT for 1 h, and rinsing in toluene. Deposits were made of one half-cycle (NPs only) up to 9 complete cycles. After deposition the samples were annealed for 1 h at 300°C in flowing N_2, which removed at least 85% of the organic compounds based on FTIR. SEM and cross-sectional TEM showed that after 9 cycles, 40% of the surface was covered with small islands consisting of clusters of Au NPs that were 10-20 nm in diameter and 20-30 nm apart from one another. AFM showed that the heights of the islands were also 20-30 nm. FTIR also showed that EDT replaced only half of the TOAB on the surface, suggesting that island growth is caused by TOAB ligands blocking binding sites. Current-voltage (IV) measurements were made by clamping two Cu terminals with a contact area of 6 mm^2 to the surface of a sample, separated by a distance of 10 mm. The film stack consisted of a) p-type Si substrate, b) 1.6 nm silicon oxide layer, c) 0.7-3 nm silane layer, and d) Au islands. A control experiment in which the Au NP islands were replaced by two 20 nm thick e-beam deposited Au films separated by a 10 mm gap yielded a sigmoidal IV curve due to current flow through the p-type Si substrate and possibly to lateral charge transfer through the APTMS monolayer. The Au NP islands increased the current flow at negative bias relative to the control. The Au NP islands could reduce the contact resistance or electrons could hop or tunnel between islands, through the underlying silane layer. Compared to the nanometer scale 1D Au NP arrays on BNNTs reported in the literature, electron transfer over such a large area found in this study could be used to scale up the class of semiconductor-free transistors that operate based on electron tunneling and could contribute to other applications that require effective local charge transfer, such as the seed layer for electro- and electroless deposition.

4:00pm **NS+BI+EM-WeA7 Nanoimprinted Amorphous Metals for Energy Applications**, *J. Schroers,* ***A.D. Taylor***, *R.C. Sekol,* Yale University*, G. Doubek,* IPEN, Brazil*, G. Kumar,* Texas Tech University*, M. Carmo,* Forschungszentrum Jülich GmbH, Germany*, F. Gittleson, N. Hardesty-Dyck,* Yale University*, S. Mukherjee*, University of North Texas **INVITED**

Here we report a unique CMOS compatible approach using bulk metallic glass $Pt_{58}Cu_{15}Ni_5P_{22}$ (Pt-BMG) [1] to create high performance fuel cell catalysts. We have shown that these materials can be nanoimprinted into ~10 nm diameter rods with aspect ratio up to 200 [2]. A nanoporous Al_2O_3 was used as a template to create the nanorod surface. The Pt-BMG is heated into the supercooled liquid region where it softens and can be thermoplastically imprinted. Under an applied pressure (ca. 50 MPa) the Pt-BMG fills the nanopores. An additional step can separate the nanorods from the reservoir [3]. The uniformly vertical nanorods are well-isolated and parallel to one another.

Our results show that these materials are highly active with lower onset potentials for CO, methanol, and ethanol oxidation [4]. In this talk we will demonstrate how these BMG systems can also serve as a platform for stategically designed catalyst systems. As a proof of concept we have modified the surface of a Pt-BMG by depositing ruthenium using underpotential deposition. We show that this approach facilitates the fabrication of multicomponent nanowires having elements outside of the glass formability with enhanced methanol oxidation beyond the initial Pt-BMG.

References:

1. Schroers, J. and W.L. Johnson, *Highly processable bulk metallic glass-forming alloys in the Pt-Co-Ni-Cu-P system.* Applied Physics Letters, 2004. **84**(18): p. 3666-3668.

2. Kumar, G., H.X. Tang, and J. Schroers, *Nanomoulding with amorphous metals.* Nature, 2009. **457**(7231): p. 868-872.

3. Schroers, J., Q. Pham, and A. Desai, *Thermoplastic forming of bulk metallic glass - A technology for MEMS and microstructure fabrication.* Journal of Microelectromechanical Systems, 2007. **16**(2): p. 240-247.

4. Carmo, M., et al., Bulk Metallic Glass Nanowire Architecture for Electrochemical Applications. Acs Nano, 2011. **5**(4): p. 2979-2983.

4:40pm **NS+BI+EM-WeA9 Submicron Cylindrical Gratings for Rotation Sensors**, ***J. Laukkanen***, University of Eastern Finland*, S. Tonchev, Y. Jourlin, S. Reynaud,* CNRS, France*, H. Hirshy, S.G. Scholz,* Cardiff University, UK*, O. Parriaux*, CNRS, France

We demonstrate a production chain for making submicron gratings on the wall of a cylinder. Gratings of this kind can be used, for example, in rotation sensors. We have converted a conventional 2D interference lithography setup into 3D setup by using a circularly symmetrical planar high index phase mask [1]. With this method, a lot smaller period is achieved than with CNC tools, which are commonly used for similar structures.

A planar phase mask was made in CVD-grown silicon nitride (Si_3N_4) on top of a quartz mask plate using electron beam lithography and reactive ion etching. Silicon nitride was chosen as a grating material because of its high refractive index and therefore ability to cancel zeroth order transmission [2]. In photolithography, a specially made glass cylinder was used as a substrate and it was coated with photoresist by dip coating. The phase mask was illuminated with radially polarized light in oblique incidence creating an interferogram on the resist coated wall of a cylinder. The produced stitchingless grating lines were over one millimeter long.

In order to be able to mass produce these cylindrical gratings a nickel mold was done using electroforming like in LIGA process [3]. The nickel mold can then be used in injection molding. With this fabrication method, we can control the exact number of lines and spaces and have a constant period over the whole round of the cylinder, which is crucial for high precision rotation sensors.

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[2] E. Gamet, A. V. Tishchenko, and O. Parriaux, "Cancellation of the zeroth order in a phase mask by mode interplay in a high index contrast binary grating," *Applied Optics*, **46**, 6719–6726 (2007).

[3] W. Bacher, W. Menz, J. Mohr, "The LIGA technique and its potential for microsystems-a survey," *Industrial Electronics, IEEE Transactions on*, **42**, 431 (1995).

5:00pm **NS+BI+EM-WeA10 DNA Assembly on Nanopatterns Created by Electron Beam Lithography**, ***A.K. Pradhan***, Norfolk State University

A major goal of nanotechnology is to couple the self-assembly (SAMs) of molecular nanostructures with conventional micro as well as nanofabrication, for instance the so-called bottom-up and top-down fabrication methods would enable us to register and recognize individual molecular nanostructures in order to integrate them electronically into functional devices. However, the integration of top-down (lithographic pattern) with bottom-up (functionalizing with synthetic chemical) approaches remains a central challenge in nanofabrication. We demonstrate that the selective self-assembly of DNA nanostructures can happen on electron beam lithographically patterned surfaces at lower energy. The fluorescent dye coupled amine modified DNA nanostructures were selectively attached to the patterned glass substrates. The optimized binding interaction between self-assembled DNA nanostructures occurred preferably at lower beam energy due to the attractive energy between the pattern and DNAs . Patterns containing self-assembled DNA molecules with dimensions as small as 2 nm in height and 68 nm in width have been successfully demonstrated. The periodicity in DNA self-assembly was observed. This technology of combination of "top-down" fabrication and "bottom-up" self-assembly may find use wherever there is a need to attach self-assembled DNA molecules in a nanometer scale patterned surface for various applications.

5:20pm **NS+BI+EM-WeA11 Organic Resist Materials for sub-20 nm Patterning: Robust Materials Enabled by Crosslinking Based Designs**, *C. Henderson, R. Lawson,* ***A. Cheshmekhani***, Georgia Institute of Technology

Future scaling of integrated circuits (IC) is in jeopardy due to a number of challenges related to both future material and process requirements that are needed to allow for fabrication of sub-20 nm IC devices. One of the most critical challenges is that of developing patterning technologies that can allow for formation of sub-20 nm patterned structures in a fast and economically viable manner. Extreme Ultraviolet Lithography (EUVL) is poised to be the successor to current 193 nm optical lithography for high

volume manufacturing (HVM) of integrated circuits. However, problems in developing sufficiently bright exposure sources for EUVL have hindered its ramp into HVM. Now that source power difficulties appear to be on a path to being addressed, the other critical problem of developing resist materials that are capable of being patterned with EUV radiation and which can produce the desired sub-20 nm patterned features must be addressed. Current chemically amplified resist material designs will be incapable of satisfying all of the patterning requirements for EUVL, and this alternative resist material designs will be needed to enable successful integration of EUVL.

The goal of our work has been to develop novel organic resist materials that can enable sub-20nm patterning using EUVL. One of the critical challenges for producing sub-20 nm organic material patterns is that conventional positive tone polymeric resists exhibit poor mechanical stability at such dimensions and are thus prone to pattern collapse during development and drying. Furthermore, photoacid diffusion in conventional positive chemically amplified resists limits their resolution. As a result, one of our design strategies has been to explore the use of molecular resists that can either be crosslinked upon to exposure to operate in a negative tone manner or which can be crosslinked and depolymerizes upon exposure to operate in a positive tone fashion. We will present our latest results on these two families of materials and will show examples of organic resists that are capable of resolving 10 nm features using 100 keV e-beam lithography and sub-20 nm features using EUVL. The detailed materials design and mechanisms underlying these capabilities will be discussed.

Thin Film
Room: 104 A - Session TF+AS+BI+EM+SE+SS-WeA

Applications of Self-Assembled Monolayers and Nano-Structured Assemblies

Moderator: M.R. Linford, Brigham Young University, H. Zuilhof, Wageningen University, Netherlands

2:00pm **TF+AS+BI+EM+SE+SS-WeA1 Enhanced Multiphoton Processes for Molecule Localization on Plasmonic Nanostructures**, ***J. Shumaker-Parry***, University of Utah **INVITED**

Plasmonic nanostructures produce enhanced optical near fields as a result of localized surface plasmon resonances (LSPRs). Tailoring of the nanostructure size, shape, and inter-structure spacing provides tuning of the LSPR properties including the near field behavior. We use two approaches to produce plasmonic architectures with enhanced fields. First, we have developed an asymmetric functionalization process to create nanoparticle assemblies by controlling the localization of molecules on the surface of the nanoparticles. The spatial localization of the molecules on the Janus-like particles lead to controlled assembly and direction of molecules into regions of enhanced near fields, a process that can be monitored through enhanced spectroscopy. The second approach we use is based on nanosphere template lithography to fabricate uniquely-shaped plasmonic nanoantennas. One example is the nanocrescent which exhibits polarization dependent LSPR responses across a broad spectral range, from the visible through the mid-infrared regions. Simulations of the LSPR response predict localized, inhomogeneous near fields around the nanocrescent antennas. We mapped the local fields of nanocrescents through an enhanced multiphoton photo-polymerization process. Local cross-linking of a photopolymer provides evidence of the near field behavior and confirms the predicted polarization-depend enhanced fields. Localized photopolymerization can be used to spatially localize molecules at the nanoscale through these enhanced fields created by the plasmonic nanoantennas.

2:40pm **TF+AS+BI+EM+SE+SS-WeA3 A Path towards Single-Electron Devices**, ***P. Campbell***, University of Texas at Dallas, *L. Caillard, O. Pluchery,* University of Pierre and Marie Curie, France, *Y.J. Chabal*, University of Texas at Dallas

As the minimum feature size in CMOS technology continues to decrease, quantum effects begin to dominate the operation of the transistors. In order to compensate for these effects, we require a new transistor design that operates based on the quantum effects present at the nanoscale. Single-electron transistors present a viable option to create smaller, more efficient transistors but a high-yield process has not yet been developed for their manufacturing.

In addition to the increasing effect of quantum mechanics, current lithographic methods face challenges in scaling below the 10 - 20 nm scale. Several proposed lithographic methods, such as direct write methods, can provide high resolution lithography, enabling the creation of transistors in the sub-10 nm region. However, direct write methods require extensive development of multi-tip approaches to achieve throughput comparable to optical lithography.

A chemical method to fabricate devices can create high performance transistors with a high throughput. The first step of this process is the deposition of a monolayer of organic molecules on a hydrogen-passivated silicon surface. Second, mono-dispersed gold nanoparticles are deposited on the surface to form a tunnel junction. The electrical properties of the sample are determined by probing the surface with scanning tunneling microscopy (STM). This results in a double-tunnel junction. By properly tailoring the nanoparticle size, organic molecule size, and STM tip-sample distance, a Coulomb staircase can be observed in the I-V curve of the junction [1].

Using a 1.7 nm thick organic molecule, evidence consistent with a Coulomb staircase is observable on a small number of spectroscopy curves. However, the electronic response of each nanoparticle is not consistent. This suggests that thermal and electronic noise play a significant role in the measurement and behavior of double-tunnel junctions. As well, the properties of the junction are influenced greatly by the quality of the interface between the substrate and organic layer and the organic layer itself. By exploring the chemistry of varying length molecules on the surface and characterizing the quality of attachment and durability of the organic layer, optimization of the samples is possible to create more reliable double tunnel junctions.

References:

[1] K. Mullen, E. Enjacob, R.C. Jaklevic, Z Schuss. I-V Characteristics of Coupled Ultrasmall-Capacitance Normal Tunnel-Junctions. Phys. Rev. B 37 (1988) 98-105.

3:20pm **TF+AS+BI+EM+SE+SS-WeA5 Chemical and Electronic Interface Formation between a Monolayer and Cobalt**, ***S. Pookpanratana***, *H.-J. Jang, L.K. Lydecker, C.A. Richter, C.A. Hacker*, National Institute of Standards and Technology (NIST)

Organic-based electronics are attractive for next-generation applications because of the wide range of possibilities in tailoring the chemical structure of molecules for a desired functionality. An emerging field is to combine the flexibility of organic materials into spintronics. While the self-assembly of molecular layers onto Au is well-studied, self-assembly does not form as readily between molecules and a ferromagnetic metal due to the lack of control of the interface composition (i. e., oxide formation). Conventional approaches to fabricate hybrid organic-metal interfaces have relied on vacuum-based physical vapor deposited organic molecules since the metal-organic interface can be better controlled. However, vacuum-based deposition of organic materials limits the manufacturing and applications of such hybrid systems making solution-based processes attractive for organic-based electronics. We have explored self-assembled monolayers (SAM) on a template-stripped Co surface to understand the molecular-metal interface from a structural, chemical, and electronic point of view.

Template-stripped Co is a method to prepare consistent surfaces that can be used in ambient conditions. First, Co is evaporated onto a molecular layer-treated Si (tSi) surface, and then the Co surface is laminated to a plastic substrate. The plastic/Co surface is stripped off of the tSi and immediately placed into SAM solution. We chose octadecanethiol (ODT) and mercaptohexadecanoic acid (MHA) as “fruit fly” molecules to self-assemble onto Co. This hybrid molecule-metal interface is investigated by using microscopy, infrared spectroscopy, and photoelectron spectroscopy to provide details of the physical, chemical, and electronic structure at that interface.

The self-assembly of ODT and MHA are directly confirmed by infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The absorbance intensities of the C-H stretches of ODT and MHA on Co are comparable to those on Au, which indicates similar packing density on both surfaces. MHA has the added complexity with both the -SH and -COOH functional groups are able to bond. Moreover, the –COOH groups also affect the Co surface by reducing the native oxide as shown by XPS. Molecular electronic junctions formed on Si by flip-chip lamination [1] show that electron transport is heavily influenced by the MHA/Co interface or Co electrode when compared to a Si/MHA/Au control device. Preliminary results suggest that SAMs on Co surfaces are a promising route for controlling the organic-ferromagnet interface for next generation devices.

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4:00pm **TF+AS+BI+EM+SE+SS-WeA7 Stability of the Molecule-Substrate Interface in SAMs Probed by SIMS – Experiments and Simulations**, *J.W. Ossowski, J. Rysz, D. Maciazek,* Jagiellonian University, Poland, *M. Krawiec,* Maria Curie-Sklodowska University, Poland, *Z. Postawa,* Jagiellonian University, Poland, *A. Terfort,* Goethe University, Germany, ***P. Cyganik***, Jagiellonian University, Poland

Self-Assembled Monolayers (SAMs) play nowadays a key role in many aspects of nanotechnology ranging from pattering and molecular electronics up to biocompatible materials. One of the key requirements for successful

use of SAMs in all of these applications is a control of their stability at the molecule-substrate interface. Analysis of this interface is however extremely difficult for technologically relevant, and therefore, more complicated SAMs. In this presentation we report extensive static secondary ion mass spectrometry (SIMS) studies on series of thiols and selenols on Au(111) substrates where structure and stability of molecule-substrate interface were systematically modified.[1] Correlating SIMS data with our previous microscopic[2,3], spectroscopic[4] and neutral mass spectrometry studies[5,6] we show that, SIMS can be successfully applied to monitor fine changes in the molecule-substrate interface stability of these model SAMs. To reveal the possible mechanism of ion-induced desorption sensitivity to the SAM-substrate interface energetics we discuss also results of our molecular-dynamic (MD) simulations of the desorption process for this system with starting structure calculated by DFT calculations.[1] Our data show that a new approach for probing the stability of molecule-substrate interface in SAMs can be proposed by using such relatively popular and fast technique as SIMS, which can be applied for virtually all complicated and technologically relevant SAMs.

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4:20pm **TF+AS+BI+EM+SE+SS-WeA8 Controlled Modification of Protein-Repelling Monomolecular Films by Ultraviolet Light: The Effect of Wavelength and Implications for Lithography**, *Y.L. Jeyachandran,* University of Heidelberg, Germany, *A. Terfort,* Frankfurt University, Germany, ***M. Zharnikov***, University of Heidelberg, Germany

Advanced lithographic techniques applied to monomolecular resists enable the fabrication of well-defined patterns of functional biomolecules, above all proteins, and specific receptors, which are the key elements of biosensors, bio-fouling analysis assays, cell studies, and tissue engineering applications. An essential element of such patterns is a protein-repelling "background" surrounding the pre-selected sensing areas and preventing non-specific adsorption of proteins beyond these regions. Here we use protein-repelling oligo(ethylene glycol) (OEG) terminated alkanethiolate (AT) monolayers on gold as matrix for the preparation of such patterns. Exposure of this matrix to ultraviolet (UV) light results in the damage of the OEG chains and photooxidation of the thiolate headgroups, which can be used for controlled tuning of protein-repelling properties within so-called UV direct writing (UVDW) approach or for the preparation of mixed OEG-AT/specific-receptor films by so-called UV-promoted exchange reaction (UVPER). Using several model systems, we studied the effect of the wavelength (254 – 390 nm) on the course and efficiency of the UVDW and UVPER processes applied to different OEG-AT matrices. The cross sections of the UV induced damage were found to decrease significantly with increasing wavelength of UV light. In accordance with this behavior, the efficiencies of both UVDW and UVPER were maximal at a wavelength of 254 nm, somewhat lower at 313 and 365 nm, and lowest at 390 nm. Both UVDW and UVPER allowed a fine tuning of protein affinity for non-specific and specific adsorption, respectively, but UVDW did not occur below a certain, wavelength-dependent threshold dose. Performing UVPER below this dose enables to suppress possible non-specific adsorption of proteins even in the case of non-complete exchange of the UV-damaged molecules of the primary OEG-AT matrix by receptor-bearing moieties. The obtained results are of direct relevance for the preparation of high-quality mixed OEG-AT/specific-receptor films and the fabrication of complex protein patterns.

4:40pm **TF+AS+BI+EM+SE+SS-WeA9 The 2D Self-Assembly of Strongly Dipolar Molecules**, ***A. Enders***, *D. Kunkel, S. Beniwal, P.A. Dowben,* University of Nebraska Lincoln, *S. Simpson, E. Zurek*, State University of New York at Buffalo

The self-assembly of organic molecules on flat metal surfaces can differ considerably from the well-known solution-based supramolecular chemistry. Substrates may set limits to the mobility of molecular adsorbates, and interactions across the organic/inorganic interface may perturb the electronic structure of the molecules and the substrate considerably. As a result, their diffusivity, the strength of chemical bonds, charge, protonation and deprotonation may all be dependent on the substrate itself. This can be exploited to engineer unique structures and properties that may not exist naturally in the respective crystalline phase.

One of the central questions in organic self-assembly is the role of an intrinsic molecular electric dipole and how the resulting electrostatic interaction competes with other chemical bonds. We studied small molecules with large intrinsic electrical dipole as model system for molecular films adsorption on surfaces for altering the interface dipole screening. For instance, we investigated the self-assembly and interface properties of zwitterionic molecules of type C6H2(…NHR)2(…O)2 (R = H, ...), adsorbed on Cu(111), Ag(111), Au(111) surfaces with scanning tunneling microscopy in UHV [1]. These molecules carry positive and negative charges on opposite parts of the molecule, resulting in a huge electric dipole of typically 10 Debye. We find that the dipole of the surface-supported molecule is decreased with respect to free species and of order of 1 - 2 Debye, depending on the substrate material. The molecules self-assemble into 2D structures upon adsorption, where the substrate-dependent strength of the dipolar interactions between the adsorbed molecules can dictate the network architecture. DFT calculations were performed to analyze adsorption geometry, charge transfer and dipole moment. By systematic comparison of the self-assembly of those molecules on different metal substrates we were able to show that the intrinsic dipole mainly plays a role in the structure formation if the interaction strength with the substrate is very weak, otherwise epitaxial fit to the substrate dictates the molecular arrangement.

5:00pm **TF+AS+BI+EM+SE+SS-WeA10 Quasicrystalline Ordering in Small-Molecule Self-Assembly**, ***N.A. Wasio***, *R.C. Quardokus, R.P. Forrest, C.S. Lent, S.A. Corcelli, J.A. Christie, K.W. Henderson, S.A. Kandel*, University of Notre Dame

Scanning tunneling microscopy was used to study self-assembly of carboxylic acid monolayers. In most cases, the formation of two strong hydrogen bonds results in dimer formation; in some others, linear catemer chains are formed. We report the observation of a five-membered catemer ring, stabilized by additional CH···O interactions available in the cyclic structure. We confirm the existence of CH···O hydrogen bonding, both with density functional theory calculations and by observing the disappearance of pentamers when molecules without suitable CH donors are used. Long-range assembly of pentamers results in a two-dimensional quasicrystalline lattice, the first observation of such structure from small-molecule self-assembly.

5:20pm **TF+AS+BI+EM+SE+SS-WeA11 Unexpected Behaviour of Liquid Wetting at the Limit of Small-Scale Surface Topography**, ***J. Knauf***, Advanced Molecular Films GmbH and RWTH Aachen University, Germany, *L. Reddemann,* Advanced Molecular Films GmbH and Universität zu Köln, Germany, *A. Böker,* RWTH Aachen University and DWI an der RWTH Aachen e.V., Germany, *K. Reihs*, Advanced Molecular Films GmbH, Germany

The size of topographic surface structures that affect wetting can be as small as sub-nanometer dimensions. As a model system we prepare monolayer from binary mixtures of 1H,1H,2H,2H-perfluoroalkyl thiols of different chain lengths on gold. Detailed characterization by static secondary ion mass spectrometry and ellipsometry confirm binary monolayer of randomly mixed constituents. Owing to their stiff helical conformation such perfluoroalkyl chains create topographic features of well-characterized sub-nanometer dimensions. As a result, surface topographies of randomly distributed long and short chains of a height difference of 1.2 Å per CF_2 group and a next neighbor distance of 5.8 Å are obtained.

We present comprehensive investigations of wetting properties of such binary monolayers of various molar fractions and chain length differences. As an example, a binary mixed monolayer from 1H,1H,2H,2H-perfluorodecyl and 1H,1H,2H,2H-perfluorododecyl thiols, thus differing by two CF_2 groups increase the advancing water contact angle from 116.0° for either one of the single component monolayer by about 2° to 117.7° for a surface of an equimolar composition of the two constituents. Such increase is considerably less than expected from simple thermodynamic models. Wenzel´s equation of wetting on rough surfaces predicts an advancing angle difference of 7°. Results of contact angles of different liquids on various sub-nanometer size topographies will be presented and discussed assuming an apparent effective reduction of surface energy at short length scales similar to results obtained from grazing-incidence X-ray scattering experiments [1].

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5:40pm **TF+AS+BI+EM+SE+SS-WeA12 The Balance between Transparency and Roughness on a Superhydrophobic Coating**, ***C. Wang***, *A. Wu, R. Lamb*, University of Melbourne, Australia

High orders of interfacial roughness are known to scatter light; as a result, superhydrophobic surfaces, which are inherently rough, generally appear

opaque. Therefore, an ideal range of roughness that can provide both superhydrophobicity and low light scattering in the visible light spectrum is a highly attractive challenge. The use of self-assembling nanoparticles is a popular choice to generate the required roughness for superhydrophobicity. While such systems offer ease of fabrication and processing, coating thickness is generally kept to a minimum to reduce light scattering, below the light scattering threshold, typically in the sub-micron scale. The degree of roughness in a sol-gel synthesized coating can be manipulated using differences in solvent polarity and vapor pressures. There is a clear trend in solvent-particle and particle-particle interaction under polar and non-polar solvents, resulting in a difference in nanoparticle cluster size[1], which contributes to light scattering. Changes in vapor pressure can also result in surface morphology formation during the drying process. We demonstrate that a simple change in solvent polarity on a sol-gel system can increase the optical transparency of a coating of thickness > 1 μm from 82-96% to 93-100% transparent in the visible spectrum. Meanwhile, the increased drying temperature from 100°C to 350°C can transform the coating's hydrophobicity to superhydrophobicity.

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Applied Surface Science
Room: 204 - Session AS+BI+EM+NL+NS+SS-ThM

Nanoparticle Surface Chemistry
Moderator: H. Zuilhof, Wageningen University, Netherlands, D.Y. Petrovykh, International Iberian Nanotechnology Laboratory, Portugal

8:00am **AS+BI+EM+NL+NS+SS-ThM1 Surface Analysis as a Critical Step in Translating Nanomaterials to Technologies**, ***D.W. Grainger***, University of Utah **INVITED**

Difficulties assessing human exposure, safety, and possible toxicity from nanotechnologies have prompted questions about how to characterize nanomaterials in various experimental test beds for predictive use. While little consensus is published about human risk/benefit analysis, this is confounded by lack of accepted, sensitive and reliable characterization methods of practical value for nanomaterials in physiological milieu. Relatively few studies are conducted on these materials in biologically relevant media to understand their surface properties and physical states (i.e., sedimentation, aggregation) prior to in vitro or in vivo exposures. Few studies have standard reference materials and analytical protocols established for comparisons to other studies. The current understanding of the fate of nanomaterials of most any size and shape, both in cell culture mediawith serum or inside the mammalian body, is poor at best. Additionally, the collective published scientific record documenting fate of nanomaterials in vivo is consistent with long known tissue-based particle filtration for micro-colloids, with far less success deliberately targeting particles to specific tissue or disease sites (i.e., <5% of a nanoparticle dose reaches a disease site).

To date, most data suggest that size reductions to the nanometer dimension have not significantly changed how nanomaterials interact with physiological systems in vivo, despite in vitro distinctions observed with proteins and in cell cultures. Connecting nanomaterials properties with how they interact with proteins and cells in vitro to affect their biodistribution in vivo allows a more rational approach to designing nanomaterials with specific biomedical and toxicity properties, and to avoid the ubiquitous non-specific tissue scavenging. This is related to materials interactions with whole blood components, including platelets, cells, and plasma proteins, producing fluid transport to tissue sites, particle binding, opsonization and aggregation. However, analytical methods for nanomaterialsare not sufficiently sensitive to study these effects in vivo to alter nanomaterials biodistribution patterns. Additionally, understanding how surface coatings, ligands and contaminants change physiological behavior requires careful analysis.

The nanotechnology field must develop improved, sensitive analytical tools and methods to drive a consensus for how nanomaterials (1) should be fully and reliably characterized for biological and biomedical purposes, and (2) how different nanomaterials properties produce either beneficial (i.e., therapeutic) or toxic responses inside complex physiological systems.

8:40am **AS+BI+EM+NL+NS+SS-ThM3 Molecular Surface Characterization of Individual Nano-objects**, *C.-K. Liang, S.V. Verkhoturov,* ***E.A. Schweikert***, Texas A&M University

The importance of surface characterization of nano-objects in dimensions below 50 nm is well recognized. Indeed the most pronounced changes in chemical reactivity are expected to occur on the smallest size nano-objects. Yet, as their size shrinks, measurement techniques are lagging. A further concern, when seeking insight into size-composition-reactivity relationships, is population heterogeneity. We present here a technique for assaying individual nano-objects. The method involves bombarding dispersed nano-objects one-by-one with nanoprojectiles specifically Au_{400}^{4+}, at hypervelocity. Their impact causes abundant emission of ionized ejecta which are identified individually for each impact by time-of-flight mass spectrometry. We will describe the characterization of surfaces and environments of nano-objects as revealed by selected grazing projectile impacts.

9:00am **AS+BI+EM+NL+NS+SS-ThM4 Towards the Effective Combination of Static and Dynamic SIMS for Nanoparticle and Biological Analyses**, ***C. Szakal***, National Institute of Standards and Technology

Static SIMS and dynamic SIMS experiments, protocols, instrumentation, and laboratory groups have largely developed in separate paths. As a result, it is common to think of certain application areas for a specific SIMS analysis, such as semiconductor depth profiling with dynamic SIMS and molecule-specific imaging with static SIMS. However, a combination of the two SIMS methodologies could generate a more complete data set by utilizing the surface-sensitive characteristics of ToF-SIMS with the enhanced signal dynamic range of large geometry (LG) dynamic SIMS. Benefits and potential pitfalls of such a combined analysis are discussed for nanoparticle surface chemistry vs. bulk measurements along with other biological application areas.

9:20am **AS+BI+EM+NL+NS+SS-ThM5 Quantitation of Protein Adsorption to Gold Nanoparticles**, ***C. Minelli,*** *N.C. Bell, A.G. Shard*, National Physical Laboratory, UK

The ability to quantitatively describe protein coronas of nanoparticles in biological fluids is highly sought for to understand protein corona formation, nanoparticle fate and their interaction with biological systems. A quantitative description of the nanoparticle biomolecular interface is challenging and chemical information along with structural and biofunctional characterization requires the use of complementary techniques.

The parallel use of different techniques provides in fact a range of complementary information of the materials under study, each technique being based on a specific physical principle. Here, we combine the use of liquid-based size measurement techniques such as Dynamic Light Scattering (DLS), Nanoparticle Tracking Analysis (NTA) and Differential Centrifugal Sedimentation (DCS), with vacuum techniques such as X-ray Photoelectron Spectroscopy (XPS) to provide quantitative information of core/shell nanoparticle systems.

We used a set of spherical gold nanoparticles having diameters from 20 nm to 80 nm and coated with different amount of Immunoglobulin G (IgG) antibodies as a model system. The shift of the nanoparticle Localized Surface Plasmon Resonance (LSPR) frequency measured by UV-Vis spectroscopy is known to relate to the amount of molecules adsorbed at nanoparticles' interface. We measured the LSPR shifts along with the nanoparticle sizes in liquid by using DLS, NTA and DCS. When the nanoparticles had a complete protein shell, shell thickness measurements were consistent for all the techniques. DCS sedimentation times showed excellent correlation with LSPR frequency shifts, indicating that analytical centrifugation can provide precise measurement of the thickness of complete protein shells on nanoparticles. However, in the low coverage regime, NTA and DLS techniques provided the best correlation with LSPR frequency shifts. By combining the information from the different techniques we estimated the amount of IgG molecules per nanoparticle as a function of the IgG concentration in solution. Data analysis in the high concentration regime suggested that nanoparticle curvature strongly influences the ability of a surface to allow the further adsorption of IgG.

Core/shell nanoparticle systems were also characterized by XPS. A methodology for the preparation of nanoparticle samples for analysis in vacuum was developed. XPS data was collected from nanoparticles of different core size and analysis provided quantitative chemical information of the nanoparticle. The combined use of XPS with liquid-based techniques for particle characterization provided quantitative chemical and structural information of core/shell nanoparticle systems.

9:40am **AS+BI+EM+NL+NS+SS-ThM6 Surface Characterization of Protein Functionalized Gold Nanoparticles**, *Y.-C. Wang, A. Rafati,* ***D.G. Castner***, University of Washington

Nanoparticles exhibit unique surface properties and require well-controlled surface properties to achieve optimum performance in complex biological or physiological fluids. Thus, there is a need to develop rigorous and detailed surface analysis methods for their characterization. The surface chemistries of oligo(ethylene glycol) (OEG) self-assembled monolayers (SAMs) on Au nanoparticle (AuNP) surfaces were characterized with x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), Fourier transform IR spectroscopy and high-sensitivity, low-energy ion scattering (HS-LEIS). The size, shape, and size distribution of the AuNPs was determined by transmission electron microscopy (TEM).

Both methoxy (CH_3O-) and hydroxyl (HO-) terminated OEG SAMs with chains containing 11 methylene and 4 ethylene glycol units were examined. ToF-SIMS clearly differentiates the two OEG SAMs based on the $C_3H_7O^+$ peak attributed to the CH_3 terminated SAM, while XPS didn't detect a significant difference between the two SAMs on the same surface. However, XPS did show a significant difference between the same SAM on different sized AuNPs. Both OEG SAMs were more densely packed on the 40 nm diameter AuNPs compared to the 14 nm diameter AuNPs. FTIR experiments indicates the methylene backbone groups are well-ordered on

all gold surfaces, but the OEG groups are more ordered on the 40 nm diameter AuNPs. Together the XPS and FTIR results suggest the OEG SAMs form a thicker and/or higher density SAMs on the 40 nm AuNPs compared to the 14nm AuNPs. HS-LEIS experiments showed the OEG SAMs on the 40 nm AuNPs were significantly thicker (2.6 nm) than the OEG SAMs on the 14 nm AuNPs (2.0 nm) and the flat Au surface (1.9 nm). The 2.6 nm thickness measured on the 40 nm AuNPs is consistent with thickness expected for a well-order OEG SAM (2.7 nm). TEM showed the 40 nm AuNPs had a larger size distribution and were less spherical compared to the 14 nm AuNPs, suggesting the shape of the AuNPs can have a significant effect on the structure and thickness of the OEG SAMs.

Protein G was immobilized onto the HO-terminated OEG SAMs via carbonyl diimidazole chemistry. ToF-SIMS analysis showed the relative intensities of characteristic amino acid fragments from Protein G varied with both the protein solution concentration and the type of surface.

10:40am **AS+BI+EM+NL+NS+SS-ThM9 Optical Rotation Measurements of Enantioselective Separation on Chiral Au Nanoparticles**, ***N. Shukla***, *N. Ondeck, N. Khosla, A.J. Gellman*, Carnegie Mellon University

Adsorption of chiral compounds on chiral surfaces is the initial step in enantioselective processes such as separations and catalysis. There has been a significant effort over the past decade aimed at the preparation of chiral nanoparticles based on metallic cores modified by chiral ligands. In principle, these can serve as the basis for enantioselective chemical processing. In this work we demonstrate a simple measurement of enantioselective adsorption on chiral metal nanoparticles using a method that can yield quantitative measures of the enantiospecific adsorption equilibrium constants [1].

The surfaces of chemically synthesized Au nanoparticles have been modified with D- or L-cysteine to render them chiral and enantioselective for adsorption of chiral molecules. Their enantioselective interaction with chiral compounds has been probed by optical rotation measurements when exposed to racemic propylene oxide. The ability of optical rotation to detect enantiospecific adsorption arises from the fact that the specific rotation of polarized light by R- and S-propylene oxide is enhanced by interaction Au nanoparticles. This effect is related to previous observations of enhanced circular dichroism by Au nanoparticles modified by chiral adsorbates. More importantly, chiral Au nanoparticles modified with either D- or L-cysteine selectively adsorb one enantiomer of propylene oxide from a solution of racemic propylene oxide, thus leaving an enantiomeric excess in the solution phase. Au nanoparticles modified with L-cysteine (D-cysteine) selectively adsorb the R-propylene oxide (S-propylene oxide). A robust model based on optical rotation data has been developed that allows extraction of the enantiospecific equilibrium constants for R- and S-PO adsorption on the chiral Au nanoparticles.

[1] N. Shukla, M.A. Bartel, A.J. Gellman "Enantioselective separation on chiral Au nanoparticles" Journal of the American Chemical Society, 132(25), (2010), 8575–8580

11:00am **AS+BI+EM+NL+NS+SS-ThM10 Monitoring the Citric Acid Content on Dialyzed Gold Nanoparticle**, *V. Spampinato, R. La Spina, D. Gilliland, L. Calzolai*, ***G. Ceccone***, *F. Rossi*, EC-JRC-IHCP, Italy

Gold nanoparticles (GNPs) are probably the most investigated metal nanomaterials due to their interesting properties. In fact, GNPs are applied in a several areas including material sciences, catalysis and biomedical diagnostics[1] Most of the applications of GNPs in the medical and biosensing fields require the development of careful purification to obtain afterwards a more efficient surface functionalization.[3,4] The process of purification is usually obtained by filtration, centrifugation and/or dialysis of the GNPs solution to remove part of the citrate or other stabilizing agents.[5,6] The citrate reduction Au(III) in water, known as Turkevich method, is one of the most used synthesis process to produce monodispersed and stable GNPs. [8] In this synthesis, the citrate is either the reducing agent and the stabilizer and it is used in large excess in comparison to the amount of gold.[9] In this work, we have investigated the stability and effect of dialysis on citrate stabilized GNPs by quantifying the content of citrate by Nuclear Magnetic Resonance (^{1}H-NMR), and by characterizing the GNPs/citrate interface chemistry using X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). In these studies, 15 nm gold nanoparticles stabilized with the citrate have been synthesized via the Turkevich process and the content of citrate was monitored at several or different cycles of dialysis against ultrapure water. These systematic studies showed a decreasing of the citrate content with the dialysis cycles. In particular, XPS and ToF-SIMS show that for low dialysis cycles the ratio Au/Na and Au/CHO increase almost linearly, while after 9 dialysis cycles a plateau is reached. A Similar trend is observed by^{1}H-NMR where the amount of citrate is quantified against an internal standard. The behavior of the GNPs at different dialysis cycles was also monitored by Centrifuge Particle Separation (CPS) and Dynamic Light Scattering (DLS) and UV-Vis spectra, revealing that several dialysis cycle result in a partial aggregation of the nanoparticles.

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11:20am **AS+BI+EM+NL+NS+SS-ThM11 Comparison of the Structure and Solution Behaviors of 20nm Silver and 20nm Silver-Shell-Gold-Core Nanocomposites in Aqueous Biological Media**, *P. Munusamy,* Pacific Northwest National Laboratory, *S. Chen, L.B. Yen,* Imperial College London, UK, *C.W. Wang, M. Engelhard,* Pacific Northwest National Laboratory, *A. Porter,* Imperial College London, UK, ***D.R. Donald***, Pacific Northwest National Laboratory

Different synthesis routes have made it possible to produce silver nanoparticles with variety of structure properties such as size, shape, and surface functionality. Synthesizing or processing silver nanoparticles under different conditions can impart variations in properties and reactivity which can influence the biological end points. In this study we have examined how silver nanoparticles of nearly identical size, as measured by dynamic light scattering, but produced with and without gold core behave in the biological media RPMI 1640 with FBS, the cell culture media used in our laboratory for in vitro nanotoxicity studies. The initial physico-chemical characterization of citrate capped nanoparticles using DLS size and surface charge measurement showed particles of average size 27nm with negative surface charge. Structure and compositional analysis using STEM and XPS confirmed the presence of gold core of size ~7nm in one set of particles. The detailed structure of the pure silver and the core-shell particles differ significantly. Based on TEM images and XRD measurements, the pure silver particles are highly crystalline, made up of ~ 15-20 nm crystallites with well-defined grain boundary or slip plane defect structures. The silver surrounding the gold core is made up of smaller highly disordered crystallites. After 24h incubation in culture media, STEM images showed that the particles with Au core dissolved significantly and non-uniformly indicating solution attack down to the gold core. In contrast, pure silver particles underwent more uniform dissolution with some indication of varying rates for different crystal faces. In addition to the dissolution of the primary particles of both types, new smaller "daughter" silver particles were observed both nearby or some distance away from the initial nanoparticles. Centrifugation followed by ICP-MS analysis of the supernatant was used to quantify the amount of dissolved silver. The dissolution extent for core-shell particles in 24h was 3 times higher than that for pure Ag. These results highlight the significance of synthesis route and sample structure on the solution behavior of similar nanoparticles in biologically relevant environmental conditions.

11:40am **AS+BI+EM+NL+NS+SS-ThM12 Influence of Carrier Gas on the Nucleation and Growth of Nb Nanoclusters Formed Through Plasma Gas Condensation**, ***K.R. Bray***, *C.Q. Jiao,* UES, Inc., *J.N. DeCerbo*, Air Force Research Laboratory

The synthesis and characterization of metallic nanoclusters is a growing field of research due to their promising catalytic, electrical, magnetic, mechanical, and optical properties. These properties generally differ from the bulk material and can be tuned by varying the nanocluster size. Transition metal clusters have received considerable interest due to their wide range of applications. Niobium has attracted attention due to observations of ferroelectric properties at low temperature. In this work, Nb nanoclusters are deposited using a plasma gas condensation process which involves the sputtering of a Nb target to create a dense metallic vapor where clusters are formed. The concept of a temperature dependent nucleation zone in conjunction with classical nucleation theory is used to describe nanocluster nucleation and growth. Changes in the nanocluster nucleation and growth are influenced through modifications of the process parameters such as carrier gas flow rate, sputter source ion current, and aggregation length. Initial data show a novel dual peak cluster distribution under select process conditions, with the smaller cluster diameter near 1 nm and the larger cluster diameter varying from 4 to 10 nm. The larger cluster appears to be a simple condensation product while data suggest the smaller cluster may be a structured cluster with a different nucleation and growth mechanism. The effects of differing argon and helium carrier gas ratios on cluster formation in conjunction with varying sputter source currents and aggregation lengths will be discussed. These results provide the opportunity for a broader understanding into the nucleation and growth of nanoclusters

as well as insights into how process parameters interact during deposition. This knowledge will enhance the ability to create nanoclusters with desired size dispersions.

Biomaterial Interfaces
Room: 201 B - Session BI+NL+NS+SS-ThM

Bio/Nano Interfaces
Moderator: G.J. Leggett, University of Sheffield

8:20am **BI+NL+NS+SS-ThM2 Utility of Lipid Membranes Assembled on Nanoparticles for Measuring Protein Membrane Interactions**, ***S.M. Reed***, University of Colorado Denver

Nanoparticles (NPs) provide a well-defined template for preparing supported lipid membranes with controlled curvature. We have coated supported lipid bilayers and hybrid membranes on silica and gold nanoparticles. The localized surface plasmon resonance (LSPR) of gold NPs can be used to monitor the assembly of lipid layers on NPs and to monitor protein lipid interactions. The gold LSPR is very sensitive to the immediate surroundings of the nanoparticle surface and therefore provides a method to monitor the coating of lipids and subsequent conversion of a supported bilayer to a hybrid membrane after the addition of hydrophobic alkanethiols. We demonstrate that both long chain (decanethiol) and short chain (propanethiol) anchors are able to form hybrid membranes and that these membranes allow for LSPR based detection of protein binding events at the membrane surface.

While many materials have been used as membrane supports, there are unmet needs in the development of membrane mimics and it remains challenging to monitor the coating process and to control the curvature of a membrane. Recent work has demonstrated that quantum dots, silica NPs, and gold NPs can be used as templates for membranes providing an opportunity to control curvature. Here, we have exploited the local refractive index sensitivity of the gold LSPR to observe the process of lipid-coating, structural rearrangement of supported membranes into hybrid membranes, and finally the binding of protein. The introduction of phosphatidylcholine (PC) to the gold NPs results in a rapid binding evidenced by a change in the wavelength of the LSPR, however, the interaction with gold is weak and the gold is not completely covered by the lipid. By adding a hydrophobic alkanethiol anchoring group, the lipids bind closer to the gold NP surface resulting in increased stability. This stability is achieved at different concentrations for short and long hydrophobic chains. When propanethiol was used it was possible to destabilize and remove the lipid coating by adding the hydrophilic thiol, beta-mercaptoethanol. This loss of membrane is observed through changes to the LSPR and increased permeability of the membrane to ions.

8:40am **BI+NL+NS+SS-ThM3 Primitive Osmosensing by Phospholipid Membranes**, *K. Oglecka,* Nanyang Technological University, Singapore*, J. Sanborn, D. Gettel,* University of California, Davis*, R. Kraut, B. Liedberg,* Nanyang Technological University, Singapore*,* ***A.N. Parikh***, University of California, Davis **INVITED**

This talk describes experimental observations of the response of multicomponent vesicles to osmotic gradients. We find that giant vesicles, consisting of phase separating lipid mixtures, immersed in hypertonic bath exhibit a Rayleigh-Plateu like pearling instability paving for elemental mechanical process of vesicular self-reproduction. When immersed in hypotonic bath, however, the response of giant vesicles comprise an unusual transitory state, characterized by damped, periodic oscillations between a microscopically phase-separated state and a uniform one. We find that this unusual oscillatory phase separation is synchronized with the cyclical patterns of membrane tension and poration, producing swell-burst cycles. Swelling, which is caused by the influx of water, raises membrane tension, thus promoting the appearance of microscopic domains. Bursting, which facilitates solute leakage, relaxes the membrane tension, breaking up large domains into those below the optical limit. This autonomous self-regulatory response – in which an external osmotic perturbation is managed by a co-ordinated and cyclical sequence of simple physical mechanisms. These mechanisms allow vesicles to sense (by domain formation) and regulate (by solute efflux) osmotic differences across their compartmental boundaries in a negative feedback loop producing a primitive form of a quasi-homeostatic regulation in a synthetic system, generated from simple components, namely, water, osmolytes, and lipids.

9:20am **BI+NL+NS+SS-ThM5 Ultrathin Poly(ethylene glycol) Films as Flexible Platform for Plasmonics and Lithography and as Precursors for Free-Standing Nanomembranes**, ***N. Meyerbröker***, *M. Zharnikov*, University of Heidelberg, Germany

We present a novel approach to prepare ultrathin, biocompatible films based on cross-linking of multi-functionalized, star-branched poly(ethylene glycols) (STAR-PEGs) with tunable film thicknesses of 4 – 200 nm. A two-component mixture of amine- and epoxy-terminated four-arm STAR-PEGs was spin-coated on a flat substrate and cross-linked chemically by gentle heating, resulting in a stable, hydrogel-like film with a density close to that of bulk PEG material. The films revealed pronounced swelling behavior, which was fully reversible and could be precisely controlled. Additionally, they provided a high affinity to citrate-stabilized gold nanoparticles (AuNP) that could be adsorbed with high densities into the PEG matrix from an aqueous solution. These novel PEG/AuNP composite films offer interesting and potentially useful optical properties. Controlling the accessibility, swelling behavior, and biorepulsive properties of the PEG films lithographically, we prepared nanocomposite patterns of metal nanoparticles and fluorophores imbedded into the PEG matrix as well as protein-affinity patterns in protein-repelling background. Further, using electron beam lithography, we succeeded to fabricate wettability patterns and to sculpture complex 3D microstructures on the PEG basis. Finally, we demonstrated that the PEG films can be separated from the substrate and exist as ultrathin, biocompatible, free-standing membranes. These membranes possess high stability and exceptional elasticity. They can be used in transmission electron microscopy experiments on sensitive biological targets and as a new type of support for the characterization of nanoparticles.

9:40am **BI+NL+NS+SS-ThM6 Miniaturized Localized Surface Plasmon Resonsance Sensing with Single Nanoparticle Arrays**, ***S. Chen***, *M. Svedendhal, T. Antosiewicz, M. Käll*, Chalmers University of Technology, Sweden

Ultrasensitive biosensing is one of the main driving forces behind the dynamic research field of plasmonics. I will show that the sensitivity of single metal nanoparticle plasmon spectroscopy can be greatly enhanced by enzymatic amplification of the refractive index footprint of individual protein molecules, so called plasmon-enhanced ELISA. The technique, which is based on generation of an optically dense precipitate catalyzed by horseradish peroxidase at the metal surface, allowed for colorimetric analysis of ultralow molecular surface coverages with a limit of detection approaching the single molecule limit. In addition I will show that by combining large arrays of well-separated gold nanoparticles fabricated by electron beam lithography (EBL) with hyper spectral imaging, spectral responses of up to 700 LSPR particles can be simultaneously studied. This allows us to obtain enough statistical significant number of spectra to further study the inhomogeneous broadening of the sensing properties of individual particles. This includes how variation in electric field enhancement over the surface of a single particle and variation in size and morphology of the enzymatic precipitate could affect the uncertainty in determining the number of enzyme molecules per particle. By combining the electromagnetic simulations with the measurements we could conclude that main sources of uncertainty come from variations in sensitivity across the surface of individual particles and between different particles. There is also a considerable uncertainty in the actual precipitate morphology produced by individual enzyme molecules. I will also discuss the possible improvement that can be done to achieve digital responses from the enzymatic amplified single particle sensing.

10:40am **BI+NL+NS+SS-ThM9 Design of Nanoscale Bionterfaces by Self-Assembly of Genetically Encoded Peptide Polymers**, ***A. Chilkoti***, Duke University **INVITED**

This talk will cover work in my laboratory over the past decade on the self-assembly of genetically encoded stimulus responsive elastin-like polypeptides (ELPs). We have exploited ELPs to create stimulus responsive nanostructures via three approaches. In the first approach, we have designed diblock ELPs with two ELP blocks with different hydrophobicity's that self-assemble into spherical micelles with an increase in temperature about the critical micellization temperature of the diblock polymer. Building on this architecture, we have incorporated histidine residues in the hydrophobic block to create a diblock ELP that self-assembles into spherical micelles with an increase in temperature, while a small drop in pH from 7.4 to 6.4 leads to micelle disassembly. In a second –chemical attachment triggered self-assembly– approach, we have shown that the attachment of multiple copies of small molecule hydrophobes to the multiple cysteine (C) residues of an ELP with the sequence $(VPGXG)_n(CGG)_8$ can drive their self-assembly into spherical micelles. In a third approach, we replace the Cys (C) with W, Y, or F, and find that oddly, this leads to the formation of stimulus responsive worms and vesicles depending on the specific residue.

These are the first examples of stimulus responsive worms and vesicles in peptide polymers.

11:20am **BI+NL+NS+SS-ThM11 Label-Free Mapping of Protein/Peptide Interactions in Complex Arrays Using Core/Shell Nanoparticle-Based Biosensors**, *H.O. Guvenc*, University of Heidelberg, Germany, *C. Schirwitz, F. Breitling*, Karlsruhe Institute of Technology, Germany, *F.R. Bischoff*, German Cancer Research Center Heidelberg, Germany, *A. Nesterov-Mueller*, Karlsruhe Institute of Technology, Germany, *V. Stadler*, PEPperPRINT GmbH, Heidelberg, Germany, *J. Wagner*, ***R. Dahint***, University of Heidelberg, Germany

The detailed analysis of biospecific interactions is of crucial importance in biomedicine, biotechnology, and pharmacology.Important applications range from medical diagnosis and drug development to the screening of the human genome and proteome. In recent years, array concepts have become very popular and powerful tools to allow for highly parallel, rapid identification of binding events. These arrays contain a multitude of different probe molecules immobilized at specific locations of an underlying substrate.

Interaction analysis is usually facilitated by labelling the potential binding partners with additional markers. Today, many of such techniques are well-established yielding considerably low detection limits and high lateral resolution. Yet, they suffer from the fact that labelling procedures are usually costly and time-consuming, that the labelling efficiency needs to be properly controlled for quantitative analysis, and that the marker itself can affect the original functionality of the molecules being studied. Moreover, the detection of low-affinity binding events is often hampered as additional washing steps and (bio)chemical reactions are required in-between the interaction and detection processes. To overcome those obstacles, strong efforts have been made to establish label-free detection schemes for interaction analysis. However, marker-free, sensitive readout of high-density arrays is still a technological challenge.

Here we report recent experiments on the label-free detection of protein/peptide interactions in complex arrays based on surface plasmon imaging with core-shell nanoparticle monolayers. Upon reflection of white light, these films exhibit a pronounced extinction spectrum which shifts to higher wavelength upon molecule binding, thus, providing a simple, sensitive and label-free detection mechanism. Variants of HA (human influenza hemagglutinin A) and FLAG epitopes with permuted amino acid sequence are synthesized in array format by means of combinatorial chemistry using a novel laser printing approach. After array preparation, the pattern is cleaved from the carrier and transferred to a biosensor surface consisting of core-shell nanoparticle films. By this means, the arrays are purified from synthesis artefacts caused by incomplete coupling reactions in the synthesis without the loss of spatial resolution. The interaction of the different peptides with their respective antibodies is quantified by the wavelength shift observed for individual peptide spots and compared to fluorescence-based interaction analysis. Based on the data we conclude on relevant amino acid sequences for an efficient antibody/epitope binding.

11:40am **BI+NL+NS+SS-ThM12 Graphene for Biosensing and Surface Functionalization**, ***P.E. Sheehan***, Naval Research Laboratory, *R. Stine*, Nova Research, *S.P. Mulvaney, J.T. Robinson, C.R. Tamanaha*, Naval Research Laboratory

Graphene, a one-atom thick sheet of sp^2 carbon, offers many intriguing possibilities in the field of molecular sensing. Its unique combination of large areas with nanometer thickness and high electrical conductivity could enable small scale device sensitivity with large scale production methods. A major benefit of using graphene is the large toolbox of well-established chemistries for incorporating chemical functionalities or specific recognition elements at the device surface. Here, we will discuss our efforts to develop graphene-based biological field-effect transistors (BioFETs), which offer sensitivity comparable to sensors made with other nanoscale materials (carbon nanotubes, nanowires), but with greatly simplified production methods common in the semiconductor industry. Devices utilizing both graphene and graphene oxide will be covered, and surface spectroscopic studies of the material modification will be discussed. Successful results for the detection of specific DNA hybridization using graphene BioFETs will also be presented. We will further discuss our efforts to use graphene as a biofunctionalized interface for a number of materials, from polymers to dielectrics to semiconductors, of interest to the biosensing community. Graphene's ultrathin nature allows its inclusion in more traditional sensing platforms as a non-intrusive functionalization layer, discreetly lending its chemical flexibility to other, more inert materials without significantly impacting the sensing device.

Scanning Probe Microscopy Focus Topic
Room: 202 C - Session SP+AS+BI+MI+NS+SS-ThM

Advances in Scanning Probe Imaging

Moderator: S. Allen, The University of Nottingham, UK, A.P. Li, Oak Ridge National Laboratory

8:00am **SP+AS+BI+MI+NS+SS-ThM1 Inelastic Imaging of Single Molecule Dynamics**, ***W. Ho***, University of California, Irvine **INVITED**

A greater part of chemistry is designed to probe the encounter of reactants to form products through a sequence of reaction steps that involve reaction complexes as intermediates. The detection of these complexes is an important step to reveal the reaction mechanisms and advance our understanding and control of chemistry. While sophisticated spectroscopic techniques have been developed to provide properties of the complexes in the energetic and temporal domains, much less is known about the spatial properties. Advances made over the last 15 years in scanning tunneling microscopy (STM) have led to direct characterization and imaging of reaction complexes that are formed by controlled manipulation of the reacting molecules to separate from each other at distances from non-interaction to those approaching the transition state. Changes in their vibrational properties can be monitored as a function of the spatial separation by inelastic electron tunneling spectroscopy (IETS) with the STM. Both spectroscopic information (vibrational energies, intensities, and lineshapes) and inelastic images can be obtained by STM-IETS. These results provide sub-THz spectral characterization and spatial visualization of chemical reactions with sub-Angstrom spatial resolution.

8:40am **SP+AS+BI+MI+NS+SS-ThM3 Tunneling Resonances Into Engineered Nanoscale Cavities on a Noble Metal Surface**, ***A. DiLullo***, *D. Acharya*, Ohio University, *N. Takeuchi*, Universidad Nacional Autónoma de México, *S.-W. Hla*, Ohio University

Variations in surface topologies such as step edges and surface defects are known to alter the electrochemical properties of the surfaces. The ability to directly alter surface topologies on the nanoscale in order to achieve desired properties is useful. We report on the direct modification of local surface topologies and the resulting changes in local electronic properties. Surface vacancies on a Ag(111) surface are created by probe manipulations using a scanning tunneling microscope operated at 78 K. Tunneling resonances, found at certain probe-sample biases, are determined by analysis of spatial height-differential mapping (dz/dV). The resonances, when considered over paths crossing the induced surface vacancies, significantly shift when comparing clean terraces to vacancy positions. These resonances originate as a result of field emission where the emitted electron has greater energy than the surface potential (work function) at the probe lateral position. By fitting these resonances to the Gundlach equation describing resonant tunneling it is possible to extract the tip work function, sample work function at probe position, and absolute tip height from the sample. The shift in resonances at vacancy locations is related to the variation in the work function due to local topology. It is important to be able to tune the work function as it plays a large role in many surface processes and properties. The created surface vacancies may then be considered local wells having work functions differing from the supporting substrate, with resonances tunable by probe manipulations, and may be useful for nanotechnological applications.

9:00am **SP+AS+BI+MI+NS+SS-ThM4 Real-space Spectroscopy and Microscopy of Tunneling Electron Induced Light Emission from Single Gold Nanoclusters**, ***S.W. Li***, *A.X. Yu, G. Czap, W. Ho*, University of California, Irvine

Historically, gold has been treasured for its beauty and permanence. In the quantum regime, gold nanoclusters gain even more reputation from their unique power as photocatalysts. To better understand the optical properties of nanoclusters, we investigated Scanning Tunneling Spectroscopy and tunneling electron induced light emission of single Au nanoclusters deposited on Al_2O_3 / NiAl(110) surface. In this electron-in-light-out experiment, optical phenomena are probed with sub-Ångström spatial resolution.

9:20am **SP+AS+BI+MI+NS+SS-ThM5 Spatial Mapping of Surface Plasmons in Nanoscale Ag Islands on Graphite using Scanning Probe Energy Loss Spectroscopy**, ***K. Bauer***, *S. Murphy, L. Tang, R.E. Palmer*, University of Birmingham, UK

A scanning STM tip operated at high voltage can be used to obtain localized spectroscopic information from surfaces via energy loss measurements [1]. In this technique, known as Scanning Probe Energy Loss Spectroscopy (SPELS), the STM tip is used as a localized source of field-emitted

electrons, which, upon backscattering from a surface, are analyzed by an energy-dispersive detector to obtain localized energy loss spectra. Characteristic surface excitations such as plasmons and excitons (as well as secondary electrons) can be probed with a spatial resolution below 50 nm and an energy resolution approaching 0.3 eV [2].

We report the development of a new generation SPELS instrument utilizing a 400-channel electron detector. This allows sufficiently fast sampling of the energy loss spectra to obtain 2D spatially-resolved maps of energy loss features in a reasonable timeframe. We demonstrate the new instrument by mapping plasmons in (thermally evaporated) Ag nano-islands on the surface of graphite and illustrate the various mechanisms give rise to the contrast obtained in the energy-resolved maps.

[1] A. Pulisciano, S.J. Park and R. E. Palmer, Appl. Phys. Lett. 93, 213109 (2008).

[2] F. Festy and R. E. Palmer, Appl. Phys. Lett. 85, 5034 (2004).

9:40am **SP+AS+BI+MI+NS+SS-ThM6 Development of a Synchrotron X-Ray Assisted STM**, ***H. Kersell***, *S.-W. Hla*,** Ohio University**, *N. Shirato, V. Rose*, Argonne National Laboratory

Scanning tunneling microscopy (STM) yields substantial information about surface properties of conductive materials by probing the electronic properties of samples under investigation. However, the nature of STM's reliance on the sample density of electronic states often limits the elemental contrast of resulting images. By targeting samples with high energy X-rays, such as those generated by a synchrotron light source, core level electrons may be excited and subsequently measured as a contribution to the tunneling current in STM. Since core level energies are chemically specific, this technique can be used to gain elemental sensitivity in STM imaging, providing enhanced understanding of molecule-substrate and intermolecular interactions. We present the development of a synchrotron-assisted STM (SXSTM), for this purpose.

10:40am **SP+AS+BI+MI+NS+SS-ThM9 High-Speed AFM Studies of Cell Membrane Dynamics**, ***A. Slade***, *S.C. Minne*, Bruker Nano Inc.

Bacterial membranes have a much more complex structure than mammalian cell membranes. As such, knowledge of bacterial membrane composition and organization, as well as characterization of the molecular-level responses to drug interactions, is critical to the development and assessment of effective antibacterial drug formulations. Cellular drug responses involve highly dynamic processes. However, the ability to image live cells with nanometer resolution on timescales relevant to dynamic cellular events has proven challenging. With traditional AFM systems, the typically longer image acquisition times required to obtain a single high-resolution image (~minutes) has limited the ability to investigate dynamic biological processes. While recent years have shown significant progress in the development of high-speed atomic force microscopy (HS-AFM), the nature of the instrumentation that has been developed has several drawbacks in specimen size, requiring small scan sizes and flat sample surfaces. As such, the majority of biologically-related HS-AFM studies have concentrated on imaging single biomolecules with little focus on using HS-AFM to examine cellular processes. With the rapidly growing antibiotics crisis, antimicrobial peptides (AmP) are increasingly being investigated as therapeutic alternatives. Key to their success is an understanding of the mechanisms by which AmPs interact with the cell membrane and facilitate cellular death. Using HS-AFM, we have obtained the first high-resolution time sequence images of the native structure of a bacterial outer membrane, obtained directly on the surface of live *Escherichia coli* cells. The increased time resolution of HS-AFM allowed us to observe dynamic changes in the nanoscale structure of the outer membrane in direct response to the AmP CM15, at timescales relevant to the mechanism of AmP-induced cell death. To understand how CM15 interacts with the bacterial inner membrane, we also conducted HS-AFM imaging on supported model membranes that mimic the composition of the inner membrane of *E. coli*. Our results revealed the formation of circular, pore-like defects within specific lipid domains upon exposure to the AmP. The results of these HS-AFM studies have provided the first opportunity to resolve the dynamics of AmP-mediated cell death in a native cell membrane environment in real-time and with nanoscale resolution.

11:00am **SP+AS+BI+MI+NS+SS-ThM10 Photothermal Excitation for Reliable and Quantitative AFM**, ***A. Labuda***, *D. Walters, D. Bocek, M. Rutgers, J. Cleveland, R. Proksch*, Asylum Research, an Oxford Instruments Company

Since the advent of atomic force microscopy, cantilevers have predominantly been driven by piezos for AC imaging and data acquisition. The ease of use of the piezo excitation method is responsible for its ubiquity. However, the well-known "forest of peaks", which is clearly observed while tuning a cantilever in liquids, renders AC imaging in liquids problematic because the peaks move around with time (see Figure). Effectively, these shifting peaks result in a setpoint that changes with time causing stability problems while AFM imaging. Furthermore, the same "forest of peaks" prevents the quantitative interpretation of forces in liquids[1], air[2], and vacuum environments[3], even if the cantilever tune looks clean. Dissipation studies in all these environments have especially suffered due to piezo excitation of the cantilever.

Photothermal excitation is an alternative method for exciting a cantilever by heating/cooling the base of the cantilever to drive the cantilever. Photothermal excitation results in a repeatable, accurate and time-stable cantilever tunes, as seen in the Figure. Therefore, the setpoint remains truly constant while imaging, preventing tip crashes, or unwanted tip retractions. A true atomic resolution image of calcite in water, shown in the inset of the Figure, were made for hours with no user intervention, testifying to the stability of photothermal excitation. Unlike other specialized drive methods, photothermal excitation is compatible with almost any cantilever and with all AFM techniques. The introduction of a blue laser into the AFM also enables several other functionalities, such as tuning the temperature of the cantilever. Furthermore, because the photothermal tune represents the true cantilever transfer function, existing AFM theories can be applied to accurately recover conservative and dissipative forces between the tip and the sample. This is especially important for force spectroscopy, dissipation studies, as well as the frequency modulation AFM techniques.

Our recent developments in perfecting photothermal excitation [4] and its benefits to the AFM community will be discussed in this talk.

[1] A. Labuda, K. Kobayashi, *et al*. AIP Advances **1**, 022136 (2011)

[2] R. Proksch and S. V Kalinin, Nanotechnology **21**, 455705 (2010)

[3] A. Labuda, Y. Miyahara, *et al*. Phys. Rev. B **84**, 125433 (2011)

11:20am **SP+AS+BI+MI+NS+SS-ThM11 Minimally Invasive AFM for Imaging Biomolecules in Liquid**, ***B.W. Hoogenboom***, University College London, UK **INVITED**

Atomic force microscopy (AFM) is a unique tool in combining nanometre spatial resolution and high temporal resolution with the ability to visualise biological molecules in their native environment, i.e., aqueous solution. Its ultimate resolution on such samples depends on the strength of the interaction between the sample and the AFM probe: Too weak an interaction means low contrast, too high an interaction usually results in molecules being distorted or dislodged. I will discuss our recent work on minimising the invasiveness of AFM in liquid, resulting among others in the first observation of the DNA double helix on a single molecule in aqueous solution [Nano Lett. 2012, 12(7), pp. 3846-3850].

Applied Surface Science
Room: 204 - Session AS+BI+EM+NL+NS+SS-ThA

Nanoparticle Surface Chemistry II
Moderator: N. Kruse, Université libre de Bruxelles, Belgium

2:00pm **AS+BI+EM+NL+NS+SS-ThA1 Fundamental Explorations of Chemical Bonding and Surface Chemistry at Graphene Interfaces**, *B.J. Schultz, V. Lee, R. Dennis, J. Aldinger, S. Henderson,* ***S. Banerjee***, University at Buffalo, The State University of New York **INVITED**

The distinctive 2D sp^2-hybridized structural framework of graphene gives rise to a unique electronic structure characterized by conical valence and conduction bands touching at the Dirac point with linear energy dispersion within ± 1 eV of the Fermi level. Given the entirely surficial geometric structure of graphene, the extent of manifestation of true Dirac physics in this material is substantially modulated by perturbations of the electronic structure as a result of interactions with charged impurities, coupling to the underlying substrate, orbital hybridization with deposited contacts, and buckling/corrugation of graphene sheets. I will focus on the results of our combined X-ray absorption spectroscopy, Raman microprobe analysis, and density functional theory studies of graphene/metal and graphene/dielectric interfaces. Depending on the nature of the transition metal and the proximity of the graphene surface, physisorption or covalent chemical bonding is observed. Studies of the hybridization of single-crystalline metal surfaces with graphene suggest clear facet selectivity. We further evidence the potential for anisotropically functionalizing only one surface of planar graphene. For dielectric interfaces, charge transfer is observed without formation of carbidic bonds. Next, I will discuss our recent results on nitrogen incorporation within graphene oxide achieved through chemical reduction or annealing under a NH_3 atmosphere. Using near-edge X-ray absorption fine structure spectroscopy in conjunction with electrical transport measurements, we have developed a detailed picture of the recovery of the electronic structure of graphene oxide upon chemical or thermal defunctionalization. I will further discuss the design of graphene—polyetherimide nanocomposites based on engineered graphene interfaces that endow remarkable corrosion protection to low alloy steel upon application as thin films.

2:40pm **AS+BI+EM+NL+NS+SS-ThA3 Structure-dependent Trends in Adsorption of CO, O_2, and H_2 on Pd and Pt Nanoparticle Catalysts**, ***H. Mistry***, *F. Behafarid, B. Roldan Cuenya*, University of Central Florida

Many important catalytic reactions have shown striking dependence on particle size and shape. Therefore, understanding structure-dependent adsorption processes using model nanoparticles is key to designing highly active and selective catalysts. Temperature-programmed desorption and x-ray absorption fine structure spectroscopy were used to study the interaction of adsorbates with Pt and Pd nanocatalyts. The binding strength of oxygen and carbon monoxide adsorbed on Pd nanoparticles supported on SiO_2/Si(111) was shown to increase with decreasing particle size. In addition, pressure-dependent changes in hydrogen coverage and structure of size- and shape- selected Pt/γ-Al_2O_3 nanoparticles were investigated.

3:00pm **AS+BI+EM+NL+NS+SS-ThA4 CO-induced Scavenging of Oxide-Supported Platinum Nanoclusters**, *N. Chaabane,* INSTN, CEA, France, *R. Lazzari,* ***J. Jupille***, INSP, UPMC and CNRS, France, *G. Renaud,* INSC, CEA, France, *EA. Soares*, ICEx-IFMG, BeloHorizonte MG, Brazil

The efficiency of oxide-supported catalysts frequently relies on the dispersion of the metallic particles whereas the optimization of the proportion of active atoms of the often precious metals involved in catalysts is an economic issue. Beyond the achievement via synthesis processes of the optimum morphology that accounts for the combination of those constraints, a great attention is paid to the phenomena which drive changes in shape, size and structure of the clusters of catalysts in running conditions. Aside the capability to resist high temperature aging, a main concern is the sustainability of catalyst particles upon exposure to reactive atmospheres. A prototypical case is the effect of CO on transition metals catalysts, of which supported platinum is a thoroughly studied example because it combines a strong practical relevance with puzzling stability behavior in the presence of CO [1]. Under CO exposure, disruption and agglomeration of supported Pt clusters were simultaneously evidenced by extended x-ray absorption fine structures, scanning tunneling microscopy and infrared spectroscopy. However, those parallel phenomena are not explained yet.

In the present work, changes in size and shape of MgO(100)-supported Pt nanoclusters were tracked *in situ* by Grazing Incidence Small-Angle X-Ray scattering (GISAXS) at CO pressures ranging from 10^{-6} to 10^{3} Pa [2]. MgO has been chosen as an archetype of non-reducible support giving rise to abrupt interfaces with platinum [3]. Between 300 K and 470 K, Pt particles smaller than a critical size of 1 nm were shown to disrupt at CO pressure as low as 10^{-1} Pa. Once formed, the disrupted particles - suggested to be carbonyl moieties - underwent scavenging by clusters larger than the critical size. Disruption and agglomeration are both consistent with a CO-driven ripening mechanism [4]. An additional agglomeration mechanism was evidenced. Upon annealing up to the desorption temperature of CO, CO-covered Pt clusters of size ranging between the critical value and 2 nm were seen to agglomerate by diffusion; this is discussed in terms of an adsorbate-induced weakening of the cluster-support bonding. Similar CO-induced mechanisms (ripening and cluster diffusion) are suggested to hold for other supported metal catalysts such as Ru, Rh and Ir.

[1] Y. Nagai et al., Catal. Today 175 (2011) 133.

[2] N. Chaâbane, R. Lazzari, J. Jupille, G. Renaud and E.A. Soares, J. Phys. Chem. C 116 (2012) 23362.

[3] J. Olander, R. Lazzari, J. Jupille, B. Mangili, J. Goniakowski and G. Renaud, Phys. Rev. B 76 (2007) 075409.

[4] R. Ouyang, J.-X. Liu and W.-X. Li, J. Am. Chem. Soc 135 (2013) 1760.

3:40pm **AS+BI+EM+NL+NS+SS-ThA6 Adsorption Energies of Cu Nanoparticles on CeO_{2-x}(111) Supports Studied by Microcalorimetry**, ***T.E. James***, *S.L. Hemmingson, C.T. Campbell*, University of Washington

The increasing demand for energy has accelerated the need to develop new and improved catalysts for existing and alternative technologies. Heterogeneous catalysts consisting of transition metal nanoparticles dispersed across oxide supports are found in solar cells, fuel cells, industrial chemical production and environmental cleanup. Fundamental understanding of these supported catalysts, such as the bond energies between the metal clusters and their supports, which is crucial to understand the sintering behavior and catalytic reactivity, is still largely missing. This work uses Cu clusters and a single-crystal ceria support as a well-defined model system to study the bond energies between metal clusters and the oxide support as a function of particle size. The adsorption energies and growth morphologies of Cu on CeO_{2-x}(111) (where x= 0.05, 0.1 or 0.2) at 100 and 300 K were investigated using single crystal adsorption microcalorimetry together with x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and sticking probability measurements. Ceria thin films (~4nm) were grown on Pt(111) single crystal. The initial heat of Cu adsorption decreased with the extent of reduction of the ceria surface. The measured heat of adsorption increases with additional Cu deposition until it reaches the Cu bulk heat of sublimation (ΔH_{sub} = 337 kJ/mol) at > 4 monolayers coverage. Interestingly, the Cu coverage required to reach ΔH_{sub} decreases as the ceria surface is reduced. These results indicate that Cu adsorbs more strongly to ceria terraces than to oxygen vacancy sites, since the primary defect for reduced ceria surfaces is oxygen vacancies, but weakens the Cu-Cu bond for particles nucleated at terraces. The growth modes of Cu on CeO_{2-x}(111) was also studied by XPS, ISS and AES. It was found that Cu grows as three dimensional particles on ceria. At 100 K the Cu particle density increased compared to 300K with a similar initial heat of adsorption, but took longer to reach the Cu heat of sublimation. The sticking probability was near unity for Cu adsorption on all these surfaces.

4:40pm **AS+BI+EM+NL+NS+SS-ThA9 Complimentary XPS and AES Analysis of MoS_3 Solid Lubricant Coatings**, ***J.R. Lince***, The Aerospace Corporation, *S.S. Alnabulsi, D.F. Paul, J.F. Moulder, J.S. Hammond*, Physical Electronics Inc.

Molybdenum disulfide (MoS_2) nanoparticles are an ideal additive in solid coating for lubricating mechanisms in vacuum environments, with widespread application in the spacecraft industry. The formation of these nanoparticles can be complex, and the use of MoS_3 nanoparticles, which are produced using a simple wet chemical synthesis is being explored as an alternate approach.[1] The use of MoS_3 as a tribological material has not been explored beyond its use as an oil additive.[2] There is new interest in investigating its potential for use in solid lubricant coatings.

To aid in the evaluation of the tribological performance of a MoS_3-formulated coating compared to MoS_2 based coatings, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are utilized as complimentary techniques for the surface characterization of the contact wear regions created on the coating surface.

The unique scanning micro-focused monochromatic x-ray source was used to provide x-ray excited secondary electron images that help reveal

topographical and surface chemical information which aid in resolving and pinpointing the analysis area of interest within the contact region of the wear track that is 50 µm to 100 µm wide. The micro-XPS results provided quantitative chemical characterization that complement high spatial resolution imaging AES analysis of the sub 100 nm molybdenum sulfide particles.

Tribometer testing showed the MoS_3-formulated coating perform similar to the MoS_2-based coatings, with similar coefficients of friction and endurances in dry nitrogen. MoS_3 nanoparticles produced using simple wet chemical synthesis, and the tribology of resin-bonded MoS_3 nanoparticle coating is comparable to similarly prepared bonded coatings containing MoS_2. The surface analysis results show a lubricating effectiveness that is consistent with the production of a thin film of MoS_2 in the contact region, with an increase in the presence of sulfide relative to polysulfide in the wear track and surface segregation of lubricating species.

We will present results of micro-area XPS and AES surface analyses on worn coatings to reveal changes in composition and chemical state of the coating surface, which might explain the observed friction results of the mechanical testing.

References

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O.P. Parenago, V.N. Bakunin, G.N. Kuz'mina, A.Yu. Suslov, and L.M. Vedeneeva, "Molybdenum Sulfide Nanoparticles as New-Type Additives to Hydrocarbon Lubricants," Doklady Chemistry, 383(1-3) (2002) 86-88.

Biomaterial Interfaces
Room: 102 B - Session BI+AS+BA+NS+SS-ThA

Biomolecules at Interfaces
Moderator: S.M. McArthur, Swinburne University of Technology, Australia

2:00pm **BI+AS+BA+NS+SS-ThA1 The Protein Resistance Properties of Hydroxy- and Methoxy-terminated Oligo(ethylene oxide) (OEO) Self-Assembled Monolayers (SAMs) to Membrane Proteins**, ***M. Walker***, National Institute of Standards and Technology (NIST), *A. Vaish, D. Vanderah*, National Institute of Standards and Technology (NIST) and Institute of Bioscience and Biotechnology Research

Spectroscopic ellipsometry was used to evaluate the resistance to protein adsorption of self-assembled monolayers (SAMs) of $HS(CH_2)_3O(CH_2CH_2O)_6M$ and $[HS(CH_2)_3]_2CHO\text{-}(CH_2CH_2O)_6M$, where M = CH_3 or H, on Au. The SAMs were exposed to fibrinogen, a soluble protein frequently used to evaluate surface protein resistance properties, and rhodopsin, an integral membrane protein. We show that the that the nature of the oligo(ethylene oxide) end group governs the extent of protein adsorption resistance of OEO SAMS to integral membrane proteins.

2:20pm **BI+AS+BA+NS+SS-ThA2 A Bottom-up Approach for Creating Biomimetic Surfaces with Defined Nanotopographic Structure and Surface Chemistry**, ***N.P. Reynolds***, *K.E. Styan, C. Easton*, CSIRO Materials Science & Engineering, Australia, *R. Mezzenga*, ETH Zürich, Switzerland, *B. Muir, P. Hartley*, CSIRO Materials Science & Engineering, Australia

Interactions of tissue cells with their local microenvironment (the extracellular matrix) can be split into three distinct categories: 1) Physical interactions, such as cellular responses to elasticity or stiffness, 2) chemical interactions, with specific epitopes contained within the extracellular matrix, and 3) topographical interactions with the nanoscale fibrous proteins that make up the majority of the extracellular matrix. In order to study how these interactions affect cell physiology *in vitro*, biomimetic substrates can be designed to reproduce these interactions. Whilst there have been multiple examples of substrates that accurately mimic chemical and physical interactions, the effects of truly biomimetic topographies are less well explored.

We show for the first time it is possible to use networks of self-assembled amyloid fibers as templates for the deposition of plasma polymers under high vacuum conditions. The nanoscale topography of the underlying amyloid networks is replicated on the top surface of the polymers with remarkable fidelity, resulting in a chemically homogenous surface with well-defined nanoscale surface features that mimic the topography of the extracellular matrix. The culture of fibroblast cells on these substrates resulted in an increased cell attachment and spreading compared to flat polymer films. We show evidence that the increase in favorable cell spreading was caused by a stabilization of adsorbed serum proteins (including fibronectin) by the nano-topography. Thus, we hypothesize that the reduced denaturation of proteins on the nano-topographical substrates results in matrix adhesion moieties (e.g. the RGD sequence) being presented to the cell membrane in a more physiological orientation. This templating technique allows for the rapid and reproducible fabrication of substrates with nanoscale biomimetic topography. We believe that such surfaces will have applications in the development of new biomaterials that will allow the routine investigation of physiological nanoscale morphology on cellular phenotype.

N.P. Reynolds et. al., "Nano-topographic surfaces with defined surface chemistries from amyloid fibril networks can control cell attachment" Biomacromolecules, **2013**, DOI: 10.1021/bm400430t.

2:40pm **BI+AS+BA+NS+SS-ThA3 Nanoscale Imaging of Peptide-Membrane Interactions**, ***P.D. Rakowska***, National Physical Laboratory, UK

Antimicrobial peptides (AMPs) are attracting growing attention as efficient anti-infective agents in the post-antibiotic era. However, the detailed molecular mechanisms of their action and precise rationale for their selectivity remain poorly understood.

Here we will present our recent findings, highlighting specific membrane-mediated mechanisms of AMPs, which we probed using a de novo designed archetypal AMP and imaged using a combination of Atomic Force Microscopy (AFM) and high-resolution Secondary Ion Mass Spectrometry (NanoSIMS). This approach provides unique information on the topography of peptide-treated membranes, obtained from AFM images, suggesting membrane changes as a result of peptide structuring and pore formation. The data is complemented by chemical imaging performed on the same samples with NanoSIMS, which revealed the precise localization of peptide molecules in the membranes.

This comparative topographical and chemical imaging gives the first evidence of antimicrobial pore expansion that was further strengthened by AFM imaging in real time in liquid, and supported by microbiological and biophysical studies as well as molecular dynamic simulations.

Relevant publication:

Rakowska, P. D., Jiang, H., Ray, S., *et al*. Nanoscale imaging reveals laterally expanding antimicrobial pores in lipid bilayers. *Proc. Natl. Acad. Sci. USA*, **2013**, 110, in press.

3:00pm **BI+AS+BA+NS+SS-ThA4 Development of Molecular Modeling Capabilities in LAMMPS Specifically Designed for the Efficient and Accurate Simulation of Biomolecule-Surface Interactions**, ***R.A. Latour***, Clemson University, *C.D. Lorenz*, King's College-London, UK

The ability to understand and predict the interactions of tethered or adsorbed biomolecules (e.g., protein, DNA, carbohydrates) at material interfaces represents a critical need for many applications in bionanotechnology and biomedical engineering. Experimental methods alone are typically very limited in terms of their ability to probe the molecular level of detail needed to quantitatively understand these types of complex interfacial interactions. As a result, biomaterial systems must often largely be designed by trial-and-error approaches. Molecular simulation methods provide an excellent means to complement experimental studies to provide theoretical assessment and predictive capability of the behavior of biomolecules at interfaces with atomic-scale resolution. These methods, however, must be specifically designed and developed for biomaterial applications. The Latour group has focused on the development of molecular simulation methods for the efficient and accurate simulation of protein-surface interactions over the past two decades, mostly involving the CHARMM molecular simulation program. Over the past year, we have focused on transitioning from CHARMM to the LAMMPS molecular simulation program for our continued development work in collaboration with the Lorenz group at King's College-London. LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator) is a fast, versatile, and highly parallelizable molecular simulation program with excellent capabilities for materials modeling. It is also freely available for download from the primary developer's website (Sandia National Laboratory, <http://lammps.sandia.gov/>). Over the past year, we have been developing new LAMMPS modules that are specifically being designed to support the efficient and accurate simulation of protein-surface interactions, with planned extension to other biomolecule systems. In this presentation, we will provide an overview of the developed capabilities in the LAMMPS program, with demonstrated applications to simulate protein-surface interactions at the atomic level. The development of these molecular simulation modules in LAMMPS has the potential to revolutionize current capabilities to accurately simulate, predict, and understand mechanisms governing biomolecule interactions at material interfaces and to serve as a valuable tool for system design.

3:40pm **BI+AS+BA+NS+SS-ThA6 Dynamic Nanomaterials for Diagnostics and Drug Delivery**, ***P. Stayton***, University of Washington **INVITED**

Our group develops stimuli-responsive nanomaterials that utilize dynamic structural and architectural transitions to enable new drug delivery and diagnostic functionalities. For drug delivery applications we are focused on opening the intracellular target universe to biologic drugs. Biologic drugs such as DNA, RNA and proteins have significant therapeutic potential, but effectively formulating and delivering them remains a widely recognized challenge. Barriers include drug stability, tissue penetration and transport, but cytoplasmic entry is a widespread barrier for those that function against intracellular disease targets. We have been developing synthetic polymeric carriers that mimic the highly efficient intracellular delivery systems found in pathogenic viruses and organisms. Another important aspect of these polymeric carriers is the development of controlled polymerization techniques to streamline bioconjugation of targeting agents and therapeutics, as well as to generate controlled carrier architectures. The carriers might open up new families of peptide, antibody or nucleic acid drug candidates that attack previously inaccessible intracellular targets. For diagnostic applications we are addressing the technology gap for making clinical assays faster and more sensitive, as well as the need for simple yet efficient sample handling techniques that concentrate dilute biomarkers for point-of-care (POC) tests. We have developed a new stimuli-responsive magnetic nanoparticle reagent system for achieving both of these goals. These new bioanalytical systems are being applied to clinical lab assays, lab card disposable devices and for non-instrumented lateral flow diagnostic platforms.

4:20pm **BI+AS+BA+NS+SS-ThA8 Determination of Orientation and Tertiary Structure of Adsorbed Protein on Material Surfaces by Chemical Modification and Peptide Mapping**, ***A.A. Thyparambil***, *Y. Wei, R.A. Latour*, Clemson University

Chemical modification of targeted amino acid residues with peptide mapping via mass spectrometry (MS) is a promising technique to provide highly detailed information on the structural shifts and orientation of adsorbed protein by revealing adsorption-induced changes in amino acid solvent accessibility. A decrease in amino acid labeling (i.e., decreased solvent accessibility) is indicative of adsorbed orientation while an increase is indicative of tertiary unfolding. However, the potential of this method for the study of adsorbed protein structure is largely undeveloped at this time. The objective of our research was therefore to develop chemical modification and peptide mapping techniques that would help identify the dominant configuration of adsorbed protein on a material surface for a range of amino acid types. By directly comparing the extent of amino acid modification (profiles) from separate batch experiments targeting different types of amino acids, a fairly detailed picture of adsorption-induced changes in adsorbed protein structure can be obtained. In our current study, when unmodified segments of the protein without the targeted amino acid from the MS results was used as an internal standard for each of the batch experiments, a common baseline to directly compare the profiles of different amino acids could be obtained. Under these conditions, the configuration of hen egg white lysozyme (HEWL) when adsorbed on fused silica glass (glass), high density polyethylene (HDPE), and poly(methyl–methacrylate) (PMMA) was mapped by directly comparing the profiles of arginine (Arg), lysine (Lys), tryptophan (Trp), and carboxylic groups (Asp, Glu, C-terminus). For each of the targeted amino acid groups, the labeling procedure did not induce significant structural shifts, which was verified by circular dichroism spectropolarimetry. The resulting quantitative differences in the profiles of targeted amino acid residues in HEWL on different surfaces under different conditions correspond to different configuration of HEWL on each adsorbent surface. The developed technique has the potential for broad application and to be expanded to other targeted amino acids, thus providing highly detailed information on the adsorbed state of protein on any given surface.

4:40pm **BI+AS+BA+NS+SS-ThA9 Exploring the Formation, Lifetime and Dissociation Statistics of Acid-Amine Bonds**, *S. Raman,* ***M. Valtiner***, Max Planck Institute für Eisenforschung GmbH, Germany

Acid-amine interactions are non-covalent, long-range interactions, contributing to the structural integrity in manmade adhesives and to serve complex life functions in several biological systems. Understanding how these interactions develop and alter over time in an aqueous environment, especially when presented across an interface, is vital when it comes to designing functional surfaces for biomedical applications. We use single molecule force spectroscopy to investigate the contact dynamics of molecular bonds under near-physiological conditions. We explore the interactions of NH_2/COOH bonds that are presented across the atomic force microscopy (AFM) tip-surface interface, with much focus on the dissociation of these bonds by studying specific signatures obtained during the force measurements[#]. Since the approach permits us to have an exquisite of control over the interface, a number of experimental parameters are varied such as the number density of the molecules, ionic strength of the surrounding medium and extension/retract speed of the tip to vary the loading rate. A statistical evaluation of the interactions and contact dynamics is discussed to assess the influence of the experimental parameters on the bond dissociation. The transition rate under zero-load conditions is calculated combining the detachment statistics and Kramer Evans theory. Our results provide new insights into the binding regime and dissociation behavior of acid-amine bonds from non-equilibrium to near-equilibrium conditions as a function of the loading rate on a logarithmic scale in aqueous environments of varying ionic concentration.

[#] M Valtiner, SH Donaldson , MA Gebbie, JN Israelachvili, J. Am. Chem. Soc., 2012, 134, pp 1746–1753.

5:00pm **BI+AS+BA+NS+SS-ThA10 Thiolene Reaction Applied to Different Metal Oxide Surfaces: Role of Short and Long PEG-terminated Chains on Biomolecules Solution Adsorption**, ***A. Galtayries***, *A. Dellinger,* Chimie ParisTech, France, *V. Semetey*, Institut Curie, France

The control of biomolecules adsorption (such as proteins) and other microorganisms is of high interest for various fields of biotechnology, such as bioanalytics, cell biology, tissue engineering and biomaterials. A simple and efficient method to control adsorption includes the use of the thiolene chemistry to form self-assembled monolayer (SAM) from commercial long (poly(ethylene glycol)) and short (oligo-ethylene glycol) terminated chains, applied on metal oxide surfaces [1].

Both on silicon, titanium and iron-chromium substrates, we selected two polymers either with short or long chains: one is adhesive, the other one is non-adhesive once in interaction with solutions of biomolecules. As regards short-chain molecules, the adhesive O-(2-Mercaptoethyl)-O′-methyl-hexa(ethylene glycol) and the adhesive O-(2-Carboxyethyl)-O′-(2-mercaptoethyl) heptaethylene glycol further activated by reaction with N-hydroxysuccinimide (NHS) were selected for grafting strategies implying full surface grafting or adhesive/non adhesive patternings (100 micrometer-large bands or half-moon surfaces). Similarly, as long-chain molecules, poly(ethylene glycol) methyl ether with an average molecular weight of 5,000 have been used, adhesive ones being NH_2-terminated.

With such molecular selection, we performed a systematic study using surface characterization techniques such as X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Infra-Red Surface Spectroscopy (ATR-IRFT or PM-IRRAS): at different steps of the grafting process, as well as after interaction with protein solutions, surface qualitative as well as quantitative information where obtained to discuss the efficiency of these molecular strategies to build biointerfaces on metal oxide surfaces.

[1] ``A Facile and Versatile Approach to Design Self-Assembled Monolayers on Glass using Thiol-ene Chemistry", B. Oberleitner, A. Dellinger, M. Déforet, A. Galtayries, A.-S. Castanet,V. Semetey, Chemical Communication, 49, 1615-1617 (2013).

5:20pm **BI+AS+BA+NS+SS-ThA11 Immobilization of Peptide-Based Stimuli-Responsive Biomolecules on Silica Surfaces**, ***L. Li***, *O. Im, J. Harris, W. Han, A. Chilkoti, G.P. López*, Duke University

The immobilization of stimuli-responsive biomacromolecules onto silica surfaces is often performed the development of silica-based biosensors, protein microarrays and supramolecular assemblies. The R5 silaffin peptide, derived from *Cylindrotheca fusiform*, is of current interest because of its capacity to induce and regulate silica precipitation at ambient conditions. In this study, we found that a fusion protein comprised of a synthetic silaffin R5 peptide and elastin-like polypeptide (ELP) bound reliably to silica particles and flat silica-based surfaces. ELPs are a class of stimuli-responsive polypeptides that undergo a reversible lower critical solution temperature (LCST) phase transition. In silaffin-ELP fusion proteins, the R5 peptides serve as silica-binding domains that immobilize ELPs onto silica, allowing its surface properties to be modulated upon change in temperature through the LCSTs of the ELPs. The attachment of silaffin-ELP to silica particles was confirmed by temperature- and time-dependent turbidity, zeta potential, and dynamic light scattering measurements. As demonstrated through zeta potential measurements, the positively charged silaffin-ELPs neutralized the negative charge on the silica particles, confirming the binding of silaffin-ELPs. Dynamic light scattering experiments revealed an increase in particle size after surface modification. The sizes of surface-modified particles also changed in response to temperature. We also investigated the absorption of silaffin-ELP on oxidized silicon wafers. The elemental composition of the protein-modified surfaces was characterized by X-ray photoelectron spectroscopy. We also used ellipsometry and atomic force microscopy (AFM) to test the thickness and roughness of the protein bound surfaces. Contact angle measurements were performed to examine the temperature-responsive nature of the surfaces. Furthermore, we demonstrated that GFP-ELP fusion protein can be adsorbed to silaffin-ELP

modified silica surface through co-aggregation above their LCSTs. A thermally triggered aggregation behavior of fluorescently-labeled silica particles was also visualized using confocal fluorescence microscopy. The results of this study demonstrated that a silaffin tag can be used to immobilize ELPs on silica surfaces such as silica particles, silicon wafers and glass slides, and that these protein-modified surfaces can be used to capture and immobilize ELPs and ELP-fusion proteins reversibly onto their surfaces. This system has potential uses in bioseparations, biomaterials, and biosensors.

5:40pm **BI+AS+BA+NS+SS-ThA12 Microfluidic Extraction and Labeling of Methylated DNA from Small Cell Populations for Single-Molecule Analysis**, ***J. Benitez***, *J. Topolancik, H. Tian, C. Wallin, V. Adiga, P. Murphy, J. Hagarman, P. Soloway, H.G. Craighead*, Cornell University

We describe a microfluidic device for the extraction, labeling, and purification of human chromosomal DNA from single cells and small cell populations. The extracted and labeled material was quantified using single-molecule fluorescence analysis in nanofluidic channels. A two-dimensional array of micropillars in a microfluidic polydimethylsiloxane (PDMS) channel was designed to capture cells. Megabase-long DNA strands released from the cell upon lysis are trapped in the micropillar array and stretched under optimal hydrodynamic flow conditions. Chromosomal DNA is immobilized in the array, while other cellular components are washed away from the channel. To assess DNA methylation, genomic DNA from different cell types was extracted using the device and labeled on-chip with methyl-CpG binding domain 1 (MBD1) protein. MBD1-bound DNA was released from the device and directly transferred to a nanofluidic channel for single-molecule detection of MBD1 molecules. Individual DNA fragments and MBD1 proteins were driven electrophoretically through the nanofluidic channels. The photon counts obtained from each MBD1 detection event are directly proportional to the total number of MBD1 molecules. By quantifying the amount of bound MBD1 molecules, the DNA methylation abundance of each cell type can be assessed and compared. This methodology provides a means for epigenetic fluorescence analysis of small cell populations with single-molecule resolution, extendable to single cells.

Graphene and Other 2D Materials Focus Topic
Room: 104 B - Session GR+AS+BI+PS+SS-ThA

Plasma Processing, Surface Chemistry, Functionalization, and Sensor Applications of 2D Materials

Moderator: P.E. Sheehan, Naval Research Laboratory

2:00pm **GR+AS+BI+PS+SS-ThA1 Carbon Monoxide-induced Reduction and Healing of Graphene Oxide**, ***S.L. Weeks***, *B. Narayanan, B.N. Jariwala*, Colorado School of Mines, *B. Macco, J.W. Weber*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology; DIFFER, Netherlands, *C.V. Ciobanu, S. Agarwal*, Colorado School of Mines

Reduction of graphene oxide (GO) has recently generated intense research interest due to the possibility of using this method to inexpensively produce large quantities of graphene. Current reductive processes rely on thermal or chemical removal of oxygen functional groups from the surface. While reduction has been demonstrated, a certain fraction of residual oxygen remains after processing with current techniques. Furthermore, the use of high process temperatures in the reduction of GO leads to the generation of defects through the loss of carbon atoms from the basal plane of graphene. The ultimate improvement in the electronic, optical, or mechanical properties of graphene that can be achieved through reduction of GO is limited by defect formation and the residual oxygen remaining after reduction through present reported methods. Here, we report the facile removal of oxygen functional groups from the surface of GO through reduction in a carbon monoxide atmosphere. Common oxygen-containing functional groups on the basal plane of GO (epoxides, hydroxyls, and ketone pairs) are removed from the surface due to the reducing action of CO. First, we have used molecular dynamics simulations and density functional theory calculations to elucidate the mechanisms of removal of these surface species by CO, and show that this reduction process proceeds without degradation of the underlying graphene sheet; CO_2 and H_2O are the only surface reaction products. We also show that the corresponding activation energy barriers for these reactions are easily surmounted at low temperatures. Second, the removal of oxygen-containing functional groups from GO by CO is confirmed experimentally using *in situ* attenuated total reflection Fourier transform infrared spectroscopy, indicating the reduction of the GO surface with CO is consistent with our atomistic-level calculations. Third, through controlled generation of defects into an otherwise pristine graphene sheet, we show that exposure to CO results in near-complete healing of the sheet as demonstrated with *ex situ* Raman spectroscopy. Thus, our results indicate CO induced reduction of GO not only proceeds without damaging the underlying sheet, but also heals defects that are produced in the production of GO via exfoliation of oxidized graphite.

2:20pm **GR+AS+BI+PS+SS-ThA2 Plasma Enhanced ALD of Hafnium Oxide on Graphene Layer with Plasma Pretreatment**, ***T. Kitajima***, *T. Nakano*, National Defense Academy of Japan

Graphene is the candidate of the future generation semiconductor material due to its high mobility of electrons and ultimately thin feature of the 2D structure. The use of graphene for CMOS technology to replace current silicon devices requires matching of each interface between the substrate, electrodes, channel, and dielectrics. Among these, growth of high dielectric constant film growth over graphene is not successful due to the chemically inert nature of the graphene surface. In order to have reactive chemical bond on graphene surface, there are trials of oxidation with ozone, etc.

Here, the effect of the oxygen plasma pretreatment on the graphene surface is examined in this study.

Graphene layer is prepared by peeling method from HOPG using adhesive tape. The domain size is 1 micron in width. (AFM topograph is shown in Fig.1) The pretreatment of the graphene surface is the exposure of O_2 ICP at 30 Pa for less than 1 min. This atomically modifies the topography (fig . 2), and the chemistry of the surface (fig . 3). The XPS analysis indicates the many of the graphene 2D bonds are replaced by C-O or C-OH bond and the defects are increased.

The growth sequence of Hafnium oxide ALD consists of the exposure of metal precursor (Tetrakis Ethyl Methyl Amino Hafnium : TEMAH) with N_2 buffer flow, N_2 purge, and O_2 ICP at 30 Pa.

The chemical composition from XPS shows the film thickness is specifically controlled by ALD cycle number and it saturates at 4th cycle owing to the limited mean free path of photoelectrons .

The initial growth stage of the film with and without plasma pretreatment is compared for 2nd ALD cycle sample . (AFM in fig . 4 and 5). With pretreatment, the surface consists of 2-5 nm width dispersed nano -islands and 20 nm width HfO_2 mesa (film) of 1nm height. Mesas are separated by base graphene surface by 10 nm pitch. Without pretreatment, the surface is covered by closely packed 5-10nm width nano-islands, around 1nm of height . This comparison indicates the oxygen bonds introduced by O_2 plasma pretreatment contribute to the chemisorption of the precursor and successful 2D growth of HfO_2 in the initial stage. In contrast, inert graphene surface without pretreatment prohibits the interconnection of the physisorbed precursor with the surface and 3D island growth is preferred.

In summary, although the domain size of the HfO_2 is limited to around 20 nm, 2D mode growth is enabled by the introduction of O_2 plasma pretreatment . Further progress is necessary on the increase of the coverage of the film, minimizing the oxidation of the base graphene layer, and reducing nano-sized islands on the film.

2:40pm **GR+AS+BI+PS+SS-ThA3 Detection of Uranium and Plutonium by Graphene-Based Nanosensors**, ***G. Sandi***, Argonne National Laboratory, *A. Bobadilla*, Texas A&M University, *A.V. Sumant, L. Ocola*, Argonne National Laboratory, *J. Seminario*, Texas A&M University, *C. Mertz, M. Kaminski*, Argonne National Laboratory

The design and fabrication of arrays of electronic molecular devices as sensors for plutonium and uranium at the nanoliter volume will be discussed. Computational calculations performed at Texas A&M University and experiments performed at Argonne National Laboratory (Center for Nanoscale Materials and Chemical Sciences and Engineering Division), will be presented. In particular, we are studying graphene, which is a vibronic, plasmonic, and electronic material for molecular circuits and sensors. The idea is to use the plasmonic features of graphene molecules in order to transfer the electrical, magnetic, vibrational, and optical characteristics of nuclear agents into the graphene plasmon, which produces an enhancement (amplification) of observable quantities as successfully done with chemical and biological agents. For nuclear agents, we have additional possibilities due to their radiation features. Theoretical simulations have shown the possible use for sensors to identify single molecules with high selectivity and sensitivity that will contribute to the miniaturization, as well as efficient transport and processing of signals using graphene based devices. It is expected that this approach will allow us not only to sense targeted agents, but also to perform chemical recognition using molecular potentials, which have become the signature at the nanoscale, perfectly suitable for detection and identification of atoms and small molecules. Maps of the molecular potentials around complexes of U and Pu allows us to distinguish their main signatures similar to those

observed in biological systems where receptors are able to distinguish to its transmitters or when a donor of electrons is able to match with an acceptor. The information obtained, especially following a supercritical nuclear event, would severely limit the list of potential actors and provide critical information to guide a proper and timely response.

Acknowledgments

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3:00pm **GR+AS+BI+PS+SS-ThA4 Damage-free Etching of Graphene using Oxygen Neutral Beam towards Edge State Control**, ***T. Okada***, *K. Igarashi, S. Samukawa*, Tohoku University, Japan

The band gap of graphene needs to be controlled for electronic device applications because it is a zero band gap semiconductor. Narrow width graphene, which is called graphene nanoribbon (GNR), has an effective band gap and solves several problems. Although there are several approaches to fabricating GNRs, top-down lithographic patterning is the most attractive method for the well-arranged GNRs required for large-scale device integration. However, conventional plasma etching always produces high density defects around the edges of the GNRs due to UV irradiation. This makes it difficult to obtain a sufficiently large band gap and the high mobility necessary for GNR-based FETs using wide GNRs (>10 nm). We developed an etching process using a damage-free neutral beam (NB) to fabricate the GNRs that can eliminate the UV irradiation to overcome this issue. We compared oxygen neutral beam etching to oxygen plasma etching within the same flux and energy conditions to clarify the defect generation mechanism at the edges of graphene.

Graphene sheets were extracted by micromechanical cleaving them from the HOPG and depositing them onto the substrate. The graphene was then etched using a stencil mask. The laser spot for taking the Raman measurement was shifted step by step to measure the defects at the edges. The Raman peaks at approximately the D-band and G-band were examined.

At the edges, the D/G ratio was increased, indicating that the defects were not generated on the plane but on the edge of the graphene. We also found that the D/G ratio on the edge etched by using oxygen NB was extremely lower than that for plasma. These results suggest that high-quality graphene edges can be easily fabricated using NB etching. The defects on the edges from the plasma etching were caused by UV radiation. Several studies have reported this defect generation on materials by high-energy UV photons during the plasma processing. Since UV photons have a non-orientation, they irradiated to the edges during etching. In contrast, in the case of neutral beam etching, damage-free etching was possible because the UV radiation was suppressed.

We concluded that NB etching is a promising candidate for GNR fabrication for high-mobility graphene transistors. In addition, this damage-less etching technique can be used for defect free formation of graphene nano structures, like nano dots and its periodic array when using the top-down process.

3:40pm **GR+AS+BI+PS+SS-ThA6 Controlling the Chemistry of Graphene**, ***S. Hernández***, *E.H. Lock*, Naval Research Laboratory, *C. Bennett*, Nova Research, *C. Junkermeier, F. Bezares, S. Tsoi*, Naval Research Laboratory, *R. Stine*, Nova Research, *J.T. Robinson, J. Caldwell, T. Reinecke, P.E. Sheehan, C.R. Tamanaha, S.G. Walton*, Naval Research Laboratory

Graphene has attracted widespread interest because of its unique structural and electronic properties. Given its pure two dimensional nature, adsorbates have a strong impact on these properties and so global chemical modification provides opportunities towards homogeneous control of graphene films. However, control over the spatial distribution of chemical moieties provides an even greater functionality in that the properties can be manipulated locally, opening up a wealth of opportunities in biosensing, plasmonics, catalysis, smart surfaces, and heterojunction devices.

Global and spatial chemical functionalization of graphene using electron beam generated plasmas will be discussed. The resulting chemical, structural, and electrical properties of the functionalized graphene as they originate for -oxygen, -fluorine, and -nitrogen functionalities will be demonstrated. This work is supported by the Naval Research Laboratory Base Program.

4:00pm **GR+AS+BI+PS+SS-ThA7 Covalent Functionalization of Graphene with Fluorine by Plasma Treatment**, ***G. Mordi***, *S. Jandhyala, S. McDonnell, R.M. Wallace, J. Kim*, The University of Texas at Dallas

As the performance of graphene based devices has continued to improve over the years (mobility, contact resistance, transconductance), the realization of novel logic devices as the BiSFET (Bi-layer Pseudospin Field-Effect Transistor) for ultra-fast switching speeds and ultra-low power consumptions may not be far off. One of the challenges in realizing BiSFET[1] is the integration of a thin (1-2 nm), low-k (~2) dielectric material which can electrically isolate the two graphene layers in which a condensate is formed and at the same time act as a tunnel barrier.

One approach for obtaining a low-k dielectric is using two dimensional materials similar to graphene which can be manufactured independently and transferred on top of graphene. Covalent functionalization of graphene is a process of adding functional groups which covalently bind to the graphene network, changing its structure from sp^2 to sp^3 hybridization resulting in opening of a band gap. Fluorination among other processes (graphene oxide[1], graphane[2]) can be used to covalently functionalize graphene. Fluorinated graphene (GrF) is an interesting material because of its atomically thin nature, thermodynamically more stable compared to graphene oxide and graphane, has a wide band gap (~3-7.5 eV) and a potentially low-k dielectric (expected to have dielectric constant of ~2)[2].

In this study we utilized fluorine based plasma (CF_4) to covalently functionalize graphene films. We established suitable CF_4 plasma exposure parameters and then investigate the conduction mechanisms across GrF based devices. Raman spectroscopy studies showed the evolution of Raman active D (~1350 cm^{-1}), G (~1595 cm^{-1}), D' (1620 cm^{-1}) and 2D (~2680 cm^{-1}) peaks as function of plasma exposure (fluorination) time. XPS studies revealed the type of bonding that exists between fluorine and carbon atoms of the graphene lattice. Conductive atomic force microscopy (C-AFM) showed the *out-of-plane* conductivity on the GrF films were significantly small compared to non-fluorinated films. *In-plane* transport characteristics of GFETs displayed two minima (or Dirac points) for short CF_4 exposures possibly attributed by both ionic and covalent doping effects simultaneously. Longer exposures result in a single minimum conductivity point possibly due to dominant covalent functionalization effects.

References

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4:20pm **GR+AS+BI+PS+SS-ThA8 Field Effect Control of Carrier Conduction in Helium Ion Irradiated Graphene**, ***S. Nakaharai***, *T. Iijima, S. Ogawa*, AIST, Japan, *S.-L. Li, K. Tsukagoshi*, NIMS, Japan, *S. Sato, N. Yokoyama*, AIST, Japan

We demonstrate the gate control of carrier conduction in graphene which is functionalized by Helium ion beam irradiation in a Helium Ion Microscope (HIM) [1]. Carrier conduction control is important for graphene application to electronics, but it has long been an obstacle to realization of graphene electronics. We found that an appropriate amount of He ion dose to graphene induced point defects which enabled gate bias control of current with an on-off ratio of two orders of magnitude at room temperature.

Helium ions were applied to graphene with ion doses from $2.2x10^{15}$ ions/cm^2 to $1.3x10^{16}$ ions/cm^2. The induced defect density was estimated by numerical calculation to be 0.2% to 1.3% [2]. The introduction of defects was confirmed by the D-mode peak of Raman spectroscopy. A series of samples with different ion doses exhibited a drastic decay of current by more than five orders of magnitude as the defect density increased from 0.2% to 1.3%. In spite of such a drastic change in current, the basic structure of graphene remained, as evidenced by G-mode peak of the Raman spectra. Room temperature current switching with an on-off ratio of two orders of magnitude was realized at a moderate defect density of 0.9%. We also found that the current exhibited an exponential decay as the irradiated region length increased from 5 to 50 nm. These results suggest that the carriers in graphene are spatially localized due to interference of waves which are scattered at the randomly distributed defect sites. A theoretical investigation of localization in a defective graphene has predicted that 1% point defects will cause a strong localization of carriers [3], which shows good agreement with our experimental results. Therefore, it should be argued that the gate control of carrier conduction is realized by a transport gap which is generated by defect-induced localization.

Since the presented technique of graphene functionalization is a "top-down" process, it is easily introduced to the fabrication process of future electron devices. We will also present the application of our ion irradiation

technique to the channel of graphene transistors [4] which achieved nearly four orders of magnitude on-off ratio at 250 K.

This research is granted by JSPS through FIRST Program initiated by CSTP.

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5:00pm **GR+AS+BI+PS+SS-ThA10 Epitaxial Graphene Oxide**, ***E. Riedo***, *A. Bongiorno*, Georgia Institute of Technology, *Y.J. Chabal*, University of Texas at Dallas, *C. Berger*, Georgia Institute of Technology, *C. Aruta*, CNR **INVITED**

Graphene and graphene-based materials hold great promise for the next generation of nanodevices. One of the most pressing issues for the technological use of graphene is the possibility to control physical and chemical properties by means of ad hoc functionalization. Thermal, chemical and optical reduction of graphene oxide have been explored as a route to produce graphene-based materials with the desired electron transport, mechanical and optical properties. Here, we demonstrate the ability to reduce graphene oxide at the nanoscale by using hot AFM tips (thermochemical nanolithography, TCNL). The resulting nanostructures have a conductivity that can be tune over 4 orders of magnitude [1]. Graphene oxide is indeed a material of great interest for its potential applications in nanoelectronics, nanoelectromechanical system, sensors, polymer composites, catalysis, energy storage devices and optics. However, the chemistry of graphene oxide and its response to external stimuli such as temperature and light are not well understood and only approximately controlled. This understanding is crucial to enable future applications of this material. We have carried over a combined experimental and density functional theory study [2] which shows that multilayer graphene oxide produced by oxidizing epitaxial graphene through the Hummers method is a metastable material whose structure and chemistry evolve at room temperature with a characteristic relaxation time of about one month. At the quasi-equilibrium, graphene oxide reaches a nearly stable reduced O/C ratio, and exhibits a structure deprived of epoxide groups and enriched in hydroxyl groups. This study shows that the structural and chemical changes are driven by the availability of hydrogen in the oxidized graphitic sheets, which favors the reduction of epoxide groups and the formation of water molecules. Furthermore, we have discovered that a mild chemical oxidation of multilayer epitaxial graphene produces uniform oxidized films showing no propensity to exfoliate. XRD measurements show that the epitaxial graphene oxide films are extremely well ordered with an interlayer distance of 10 Å [3].

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Nanoparticle-Liquid Interfaces Focus Topic
Room: 201 B - Session NL+AS+BI-ThA

Nanoparticles with Proteins and Cells: Modelling and Measurement
Moderator: D.G. Castner, University of Washington

2:00pm **NL+AS+BI-ThA1 Nanoscale Interface Between Engineered Matter and Living Organisms: Understanding the Biological Identity of Nanosized Materials**, ***K. Dawson***, University College, Dublin **INVITED**

Nanoscale materials can interact with living organisms in a qualitatively different manner than small molecules. Crucially, biological phenomena such as immune clearance, cellular uptake and biological barrier crossing are all determined by processes on the nanometer scale. Harnessing these endogeneous biological processes (for example in creation of new nanomedicines or nanodiagnostics) will therefore require us to work on the nanoscale. This ensures that nanoscience, biology and medicine will be intimately connected for generations to come, and may well provide the best hope of tacking currently intractable diseases. These same scientific observations lead to widespread concern about the potential safety of nanomaterials in general. Early unfocussed concerns have diminished, leaving a more disciplined and balanced scientific dialogue. In particular a growing interest in understanding the fundamental principles of bionanointeractions may offer insight into potential hazard, as well as the basis for therapeutic use. Whilst nanoparticle size is important, the detailed nature of the nanoparticle interface is key to understanding interactions with living organisms. This interface may be quite complex, involving also adsorbed proteins from the biological fluid (blood, or other), leading to a 'protein corona' on the nanoparticle surface that determines its "biological identity."We discuss how this corona is formed, how it is a determining feature in biological interactions, and indeed how in many cases can undermine efforts at targeting nanoparticles using simple grafting strategies. Thus, nanoparticle interactions with living organisms cannot be fully understood without explicitly accounting for the interactions with its surroundings, i.e. the nature of the corona.

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2:40pm **NL+AS+BI-ThA3 *In Silico* Modelling and Prediction of the Biological Effects of Nanoparticles**, ***D.A. Winkler***, *V.C. Epa*, *F.R. Burden*, CSIRO Materials Science & Engineering, Australia, *C. Tassa*, *R. Weissleder*, Harvard Medical Center, *S. Shaw*, Massachusetts General Hospital and Harvard Medical School **INVITED**

Products are increasingly incorporating nanomaterials because of their superior properties. It is estimated that 50,000 products will contain nanomaterials by 2015. However, we have a poor understanding of their potential adverse effects on workers, the public, and the environment. To assess risk, regulatory authorities need more experimental testing of nanoparticles. Computational models play a complementary role to experiments in allowing rapid prediction of potential toxicities of new and modified nanomaterials. We have generated quantitative, predictive models of cellular uptake and apoptosis induced by surface modified metal iron oxide nanoparticles for several cell types using sparse feature selection and optimal machine learning methods. We illustrate the potential of computational methods to make a contribution to nanosafety.

3:40pm **NL+AS+BI-ThA6 Quantitative Characterization of Bacterial Cell Loading with Nanoparticles**, *C. Sousa*, *D. Sequeira*, *P.M. Martins*, University of Minho, Portugal, *Y.V. Kolen'ko*, International Iberian Nanotechnology Laboratory, Portugal, *S. Lanceros-Méndez*, University of Minho, Portugal, ***D.Y. Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

The primary analytical challenge in characterizing bacterial cells loaded with nanoparticles (NPs) is that the various methods that are traditionally used to measure cells or NPs separately are not readily applied to the mixed samples. These complex samples may contain, for example, a mixture of free NPs, NP-loaded cells, and cells without NPs, while the relative concentrations of NPs and cells or the average number of NPs loaded in one cell is not always known or readily established. Accordingly, methods for separating the different sample components have to be developed and validated before the component of interest (NP-loaded cells in most cases) can be characterized. The final challenge is determining the localization of NPs in and around the cells, as for some applications in sensing and nanomedicine NPs bound to cells externally can be the goal, whereas for exploiting physical properties of NPs, e.g., to induce hyperthermia, maximizing the internalization of NPs by cells can be advantageous.

Our approach to investigating these complex analytical challenges is based on using model systems that are amendable to quantitative characterization by complementary methods, both separately and when mixed as indicated above. Specifically, we are using *Staphyloccus aureus* as model bacterial cells, in part because the typical 500 nm diameter of *S. aureus* cells is within the size range of NP aggregates or large NPs, therefore, the same microscopy and spectroscopy methods can be applied to both components of mixed cell-NP samples. We use gold NPs as the primary model NPs because the strong plasmon peak enables their characterization in solution, while the high density and atomic number of gold can be helpful during separation and for characterization by electron microscopy and spectroscopy. Superparamagnetic iron-oxide NPs with different organic

shells are used as a second type of model NPs. We will describe the use of multiple complementary microscopy and spectroscopy techniques for developing, validating, and quantifying protocols for cell-NP separation and for characterization of cell loading by NPs.

4:00pm **NL+AS+BI-ThA7 Protein-Corona: A New Gateway to Disease Therapeutics**, ***K. Giri***, *P. Mukherjee, M. Zimmermann, S. Khader, B. Madden, D. McCormick*, Mayo Clinic

Nanomedicine is a burgeoning field with immense potential in disease therapeutics, diagnosis and imaging. However, an inevitable phenomenon regarding the use of nanoparticles (NPs) *in vivo* is the adsorption of proteins to its surface to form a layer called the "protein corona". The concept of synthetic vs. biological identity of the NPs has emerged. Studies have reported that the acquired biological identity of NPs due to its protein corona influences not just the interaction of the NPs with its targets but also its fate. Among all the NPs that are currently being investigated in nanomedicine, gold nanoparticles (GNPs) are unique in that they posses strong affinity to bind to SH and NH2 containing molecules. Therefore, proteins by virtue of having cysteine and lysine residues function as unique substrates to bind to GNPs. We hypothesize that the proteome and secretome of cancer cells may include low abundance proteins that escape detection by conventional methods. Enrichment and identification of these proteins may play a critical role in understanding the pathophysiology of disease development and open new avenues for treatment. Our aim was to study the formation of protein corona on GNP surface as a unique way to enrich and identify low abundance proteins that can serve as new therapeutic targets for ovarian cancer. Understanding the interaction of proteins on GNP surface is important as it will guide modulation of protein corona formation for protein enrichment based on physicochemical properties and structure. Here, we present a systematic study of protein corona using 20 nm GNPs. We studied the binding of proteins from lysates derived from two ovarian cell lines, namely OSE (non-cancerous) and A2780 (cancerous). We followed the evolution of the corona for 24 hrs to account for the dynamic and competitive binding of proteins on the NP surface. We characterized the corona at 5 mins, 15 mins, 1hr, 6hrs and 24 hrs using UV-vis spectroscopy, dynamic light scattering, electron microscopy and ζ-potential measurements and identified corona constituents by mass spectroscopy. We focused on understanding what drives protein adsorption to the NP surface. Lastly, we identified low abundance proteins from the A2780 cell line that were enriched on GNP surface as a proof of concept study to demonstrate that protein corona can be effectively utilized for study of disease and its therapeutics.

Scanning Probe Microscopy Focus Topic
Room: 202 C - Session SP+AS+BI+EM+MI+NS+SE+SS-ThA

Probe-sample Interactions, Nano-manipulation and Emerging Instrument Formats

2:00pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA1 Antibody Movement on Regular Antigen Clusters: Fab Arms are Made for Walking**, *J. Preiner,* Johannes Kepler Univ. & Ctr for Adv. Bioanalysis GmbH, Austria, *N. Kodera,* Kanazawa Univ., Japan, *J. Tang,* Chinese Academy of Sciences, *A. Ebner,* Johannes Kepler Univ., Austria, *M. Brameshuber,* Vienna Univ. of Tech., Austria, *D. Blaas,* Medical Univ. of Vienna, Austria, *N. Ilk,* Univ. of Natural Resources & Applied Life Sci. Vienna, Austria, *H.J. Gruber,* Johannes Kepler Univ., Austria, *T. Ando,* Kanazawa Univ., Japan, ***P. Hinterdorfer***, Johannes Kepler Univ. & Ctr for Adv. Bioanalysis GmbH, Austria **INVITED**

Antibodies are key molecules for the immune system of vertebrates. The Y-shaped IgGs exhibit C2-symmetry; their Fc stem is connected to two identical Fab arms binding antigens. The Fc part is recognized by the complement system and by phagocytic cells. Antibodies can be considered molecular calipers; bivalent binding of the two Fab arms to adjacent antigens can only occur within a distance of roughly 6 to 12 nm. This leads to much higher avidity and slower dissociation rates as compared to monovalent binding. Here we show that antibodies exhibit "bipedal" walking on antigenic surfaces and static binding of both Fab arms of an antibody may hold true only for a time scale of ~ 0.04 s. The walking speed depends on the lateral spacing and symmetry of the antigens. On 2D-crystalline surfaces, such as found on bacteria and viruses, steric strain thus appears to be the main reason for short-lived bivalent binding. Importantly, the collision between randomly walking antibodies was seen to reduce their motional freedom. It leads to formation of transient antibody clusters even at low antibody density. Interestingly, such assemblies are known nucleation sites for docking of the complement system and/or phagocytes.

2:40pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA3 Development of a Novel Single-Molecule Force Based Approach for Fragment Screening**, ***G.A. Milson***, University of Nottingham, UK

The discovery and development of new chemical entities is complex and time consuming, and of great expense to the pharmaceutical industry[1]. High throughput screening (HTS) is the main method used for lead identification, allowing significant numbers of compounds to be tested. However, productivity levels are still below those desired[2]. Due to this, interest in a relatively new process termed fragment based drug discovery (FBDD) has developed[3]. The FBDD process starts from small, efficiently binding fragments elaborated to more drug-like molecules[4]. However, with fragments being smaller components of the traditionally screened small molecules they have lower affinities and as a result require sensitive detection systems[5].

It has been proposed that the atomic force microscope (AFM) could be used as a novel system in fragment screening. The AFM benefits from the ability to probe single molecular interactions[6] using only small volumes of solution that need not be of high purity. Single molecule force recognition spectroscopy (SMFRS) is the commonly termed process where an AFM tip is functionalised with probe molecules that are known to recognise specific target molecules on the opposing surface. Fragments can theoretically be screened against their potential target on the surface and if they bind will block the natural ligand on the tip from occupying the active site.

Here, the well-characterised interaction between streptavidin and biotin was used as a model in which fragments of biotin were screened using an AFM probe functionalized with a biotin-mimetic peptide. It was seen that the AFM was capable of measuring the specific interaction between the biotin mimetic peptide and streptavidin. Each competition assay worked well, with the peptide-streptavidin interaction being blocked by fragments in a concentration dependent manner. Analysis of the percentage adhesion-versus-concentration data resulted in a ranking of the fragments, which matched their known or measured affinities to streptavidin. Despite the fact that this is still in the early stages of development, the results are promising and it is hoped that with further development the approach will be introduced into drug discovery fragment screening methods.

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3:00pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA4 Popping Nano-Balloons on TiO_2(110) Surface with the STM Tip**, ***D.V. Potapenko***, *Z. Li, R.M. Osgood*, Columbia University

Argon-filled subsurface nano-cavities can be created on TiO_2 rutile(110) surface by the means of Ar-ion bombardment combined with temperature treatment of the sample. The presence of the nano-cavities is manifested by the elliptical protrusions on the surface up to 1 nm high and 5 – 30 nm wide. We have developed a micromechanical model that can predict the shape and the depth of individual nano-cavities from the geometry of the corresponding protrusions. To evaluate the validity of the model 7 – 9 V, 1 – 10 ms voltage pulses from the STM tip were used to cause controllable explosions of the nano-cavities, thus allowing the direct independent measurements of their depth. The explosions are caused by the combination of local heating due to the voltage pulse and the high mechanical strain of the TiO_2 crystal lattice in the volume of the protrusion. We discuss the general mechanisms of the nanoscale surface modification produced by voltage pulses from the STM tip and show that at certain conditions the mechanical contact between the tip and the surface occurs. This work is an example of an unusual application of scanning probe microscopy for deep subsurface exploration.

3:40pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA6 Manipulating Magnetism One Atom at a Time**, ***S. Loth***, Center for Free-Electron Laser Science, Germany **INVITED**

Magnetic materials consist of atoms that interact very locally – often on atomic length scales. In nanoscopic systems the details of these interactions become increasingly important. We use scanning tunneling microscopy to test how far classical concepts of magnetism can be extended into the nanoworld and how they emerge from the quantum mechanical behavior of individual spins.

We have developed a complete toolset to explore magnetization dynamics in artificial few-atom nanostructures:

Magnetic atoms can be assembled into precisely defined arrays by atom manipulation with the STM tip. The atomic spins interact with each other and form collective magnetic states that can be tailored by modifying the atomic arrangements. Elastic and inelastic electron tunneling spectroscopy is used to quantify magnetic properties such as excitation energies, anisotropy barriers and spin-polarization as the nanostructure is being built up [1]. Crucial information on the stability of a nanostructure and influence of the environment can be obtained from the spin system's dynamical response to an external stimulus. For this purpose we use an all-electronic pump probe measurement scheme that excites the nanostructure repeatedly by spin-transfer torque and measures its response by spin-polarized tunneling [2].

With this technique we identified a new route to create stable magnetic states using antiferromagnetic spin-spin interaction. While individual Fe atoms exhibit a spin relaxation time on the order of 1 ns, linear antiferromagnetic chains with as few as eight Fe atoms show magnetic states that are stable for several minutes [3]. This dramatic change in dynamic behavior is indicative of a cross-over from quantum mechanical spin states to a ground state with classical magnetic order.

These experiments show a promising route towards rapid prototyping of quantum magnetic spin structures with control over static and dynamic properties by atom assembly in the STM.

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4:20pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA8 High-speed AFM with a Light Touch**, ***M. Miles***, *R. Harniman, D.J. Phillips, L.M. Picco, O. Payton, M. Antognozzi, S. Simpson, S. Hanna, D.J. Engledew,* University of Bristol, UK, *G. Gibson, R. Bowman, M.J. Padgett*, University of Glasgow, UK **INVITED**

AFM offers unique characteristics amongst microscopy techniques, and offers many benefits such has high-resolution 3D imaging in many environments including liquids. However, there are three areas in which conventional AFM has limitations: (i) a low imaging rate, (ii) the probe-sample force interaction, and (iii) the planar nature of the sample. We are developing two high-speed force microscopy techniques to overcome the first two of these, (i) and (ii).

(i) One high-speed AFM (HS AFM) technique is a DC mode in which an automatic feedback mechanism essentially arising from the hydrodynamics of the situation maintains a tip-specimen separation of about 1 nm. This technique routinely allows video-rate imaging and has achieved imaging at over 1000 fps. Damage to specimens resulting from this high-speed DC-mode imaging is surprisingly less than at normal speeds. The behavior of the cantilever and tip at these high velocities has been investigated and super lubricity is a key component in the success of this technique [1,2].

(ii) The second high-speed force microscope is a non-contact method based on shear-force microscopy (ShFM). In this HS ShFM, a vertically-oriented, laterally-oscillating probe detects the sample surface at about 1 nm from it as a result of the change in the mechanical properties of the water confined between the probe tip and the sample. With this technique, very low normal forces are applied to the specimen. Information on the molecular water layers as a function of position [3,4].

(iii) AFMs require planar samples because the probe scans in a plane. The tip only 'sees' the sample from above. We have overcome this limitation by steering the tip of a nanorod in a three dimensional scan with six degrees of freedom using holographically generated traps such that it is possible to scan around a sample from any direction. We use various probe types: including silica nanorods, rod-like diatoms, and two-photon polymerized 3D structures [5,6].

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5:00pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA10 Multimodal and Multispectral Nano-imaging: Accessing the Structure Underlying the Function of Polymers, organic Photovoltaics, and Biomaterials**, ***M.B. Raschke***, University of Colorado at Boulder **INVITED**

The properties of many functional soft-matter systems, including polymer heterostructures, organic photovoltaics, and biomembranes are typically defined on the mesoscopic few nm to sub-micron scale. Scattering scanning near-field optical microscopy (s-SNOM) has demonstrated its ability to access the relevant spatial regime. In combination with IR-vibrational spectroscopy s-SNOM provides molecular structural information. However, a yet higher degree of specificity, sensitivity, and selectivity with respect to specific molecular functional features is desired. We will discuss the combination of scattering scanning near-field optical microscopy (s-SNOM) with other nano-optical and scanning probe modalities. That together with the multi-spectral features of different coherent and incoherent IR sources including tunable continuous-wave lasers, femtosecond sources, broadband synchrotron radiation, and thermal near-field radiation provides the desired enhanced dynamic range to probe at the level of the intra- and intermolecular interaction. This results in a unprecedented degree of specificity, sensitivity, and selectivity with respect to specific molecular functional features, as we will discuss for several specific block-copolymer, organic photovoltaic, protein, self-assembled monolayer, and biomineral systems we investigated.

5:40pm **SP+AS+BI+EM+MI+NS+SE+SS-ThA12 Mapping Local Dipole Domains within Two-Dimensional Plastic Lattices**, ***J.C. Thomas,*** *J.J. Schwartz, H.S. Auluck, G. Tran, J. Gilles, S. Osher,* University of California at Los Angeles, *C.A. Mirkin,* Northwestern University, *P.S. Weiss*, University of California at Los Angeles

We have observed aligned dipoles forming two-dimensional plastic lattices in self-assembled monolayers of carboranethiols on Au{111}. We have used scanning tunneling microscopy (STM) and simultaneously acquired local barrier height images of 9,12-dicarba-*closo*-dodecaborane *o*-9-carboranethiol (**O9**) monolayers on Au{111} at 4K in extreme high vacuum to determine the local structures and dipole orientations within the monolayers. The molecular structure of **O9** is that of a symmetric cage; a two-dimensional plastic lattice of aligned dipoles is formed through favorable intermolecular dipole-dipole interactions after chemisorption. Local barrier height images juxtaposed with the simultaneously recorded topography reveal directional dipole offsets within domains. New imaging analysis methods were used to overlay the multimodal data and determine molecular dipole orientations. We employ Monte Carlo simulations to model the dipole-dipole interactions, and to predict alignment at low temperature. We compare and contrast topographic and simultaneously acquired local barrier height images of 1,7-dicarba-*closo*-dodecaborane *m*-1-carboranethiol (**M9**) on Au{[111} in which the largest dipole is due to the sulfur-gold bond (as opposed to the cage) and is aligned to topographic maxima in STM images.

Scanning Probe Microscopy Focus Topic
Room: Hall B - Session SP+AS+BI+NS-ThP

Scanning Probe Microscopy Poster Session
Moderator: S. Allen, The University of Nottingham, UK, A.P. Li, Oak Ridge National Laboratory

SP+AS+BI+NS-ThP1 Vision Sensing Based Drift Measurement and Compensation in Real Time for Atomic Force Microscope, ***Y. Wang***, Beihang University, China, *H. Wang*, The Ohio State University, *S. Bi*, Beihang University, China

Atomic force microscope (AFM) is unique in its capability in measuring deformation and force in subnanometers and has been a crucial tool in nanoscale science and technology since its invention. However, mechanical drift between AFM cantilevers and sample surfaces limits its applications, especially for some biological experiments which require long time measurement. In this study, the mechanical drift is obtained in real time by simultaneously measuring the *z* position of AFM cantilevers and sample surfaces through an off-focus image processing based vision sensing method. In this method, the *z* position of a micro bead is measured by processing the off-focus images of the bead with an optical microscope. To get the *z* position of an AFM cantilever, the cantilever is first fabricated with focused ion beam (FIB) and a micro bead is attached to the end of the cantilever. Another bead is placed on a transparent sample substrate. The *z* positions of the AFM cantilever and the sample surface can be simultaneously obtained through measuring the *z* position for the beads at end of the AFM cantilever and the sample surface, respectively. The mechanical drift between the cantilever and sample surface can be obtained and then compensated in real time.

SP+AS+BI+NS-ThP2 Rapid Near-Field Infrared Spectroscopy Using an External Cavity Quantum Cascade Laser, *I.M. Craig, M.S. Taubman, M.C. Phillips,* ***A.S. Lea***, Pacific Northwest National Laboratory, *M.B. Raschke*, University of Colorado at Boulder

Scattering scanning near-field optical microscopy (*s*-SNOM) is an apertureless superfocusing technique that uses the antenna properties of a conducting atomic force microscope (AFM) tip to achieve infrared spatial resolution below the diffraction limit. The instrument can be used either in imaging mode, where a fixed wavelength light source is tuned to a molecular resonance and the AFM raster scans an image, or in spectroscopy mode where the AFM is held stationary over a feature of interest and the light frequency is varied to obtain a spectrum. In either case, a strong, stable, coherent infrared source is required. Here we demonstrate the integration of a broadly tunable external cavity quantum cascade laser (ECQCL) into a *s*-SNOM and use it to obtain infrared spectra of microcrystals adsorbed onto gold substrates.

Residues of explosive compounds PETN, RDX, and tetryl were deposited onto gold substrates. *s*-SNOM experiments were performed in the 1260–1400 cm^{-1} tuning range of the ECQCL, corresponding to the NO_2 vibrational fingerprint region. Chemical imaging with fixed wavelength tuned to a molecular resonance allows mapping of species distributions a spatial resolution of ↑ 25 nm. Vibrational infrared spectra are then collected on individual chemical domains with a collection area of ↑ 500 nm^2. Acquisition times of less than 6 min with SNR of >50 and 0.2 cm^{-1} spectral resolution are possible. Spectra are compared to ensemble averaged far-field infrared reflection-absorption spectroscopy (IRRAS) results.

SP+AS+BI+NS-ThP3 Ferritin-based Magnetic Force Microscopic Probe with Very High Resolution, ***N. Chung***, Korea Research Institute of Standards and Science, Republic of Korea, *D.H. Kim, J.W. Park*, Pohang University of Science and Technology, Republic of Korea

A single-molecule ferritin picking up process was realized with the use of AFM, which was enhanced by employing controlled dendron surface chemistry. The approach enabled the placement of a single ferritin protein molecule at the very end of an AFM tip. When used for magnetic force microscopy (MFM) imaging, the tips were able to detect magnetic interactions of approximately 10 nm sized magnetic nanoparticles. The single ferritin tip also showed the characteristics of a "multifunctional" MFM probe that can sense the magnetic force from magnetic materials as well as detect the biomolecular interaction force with DNAs on the surface. The multifunctional tip enabled us not only to investigate the specific molecular interaction but also to image the magnetic interaction between the probe and the substrate, in addition to allowing the common capability of topographic imaging. Because the protein engineering of ferritin and the supporting coordination and conjugation chemistry are well-established, we envisage that it would be straightforward to extend this approach to the development of various single magnetic particle MFM probes of different compositions and sizes.

Nanoparticle-Liquid Interfaces Focus Topic
Room: 201 B - Session NL+AS+BI+SA-FrM

Emerging Methods to Identify and Measure Nanomaterials in Biological Environments

Moderator: G. Ceccone, European Commission, Joint Research Centre, IHCP, Italy

8:20am **NL+AS+BI+SA-FrM1 3D Views of Hydrated Biological Cells with Soft X-ray Tomography**, ***C.A. Larabell***, University of California, San Francisco **INVITED**

SXT is similar in concept to the well-established medical diagnostic technique, computed axial tomography (CAT), except SXT is capable of imaging with a spatial resolution of 50 nm, or better. We examine whole, hydrated cells (between 10-15 μm thick), eliminating the need for time-consuming and potentially artifact-inducing embedding and sectioning procedures. Cells are rapidly frozen then imaged using photons with energies between the K shell absorption edges of carbon (284 eV, λ=4.4 nm) and oxygen (543 eV, λ=2.3 nm). In this energy range, photons readily penetrate the aqueous environment while encountering significant absorption from carbon- and nitrogen-containing organic material. Consequently organic material absorbs approximately an order of magnitude more strongly than water, producing a quantifiable natural contrast image of cellular structures. By collecting images from multiple angles through 360 degrees of rotation, SXT reconstructions yield information at isotropic resolution.

Images are formed using unique optics called zone plates (ZP). An X-ray ZP optic consists of a number of concentric nanostructured metal rings, or zones, formed on a thin X-ray transmissive silicon nitride membrane. The width of the outermost ring determines the spatial resolution of the ZP lens, whereas the thickness of the rings determines the focusing efficiency. In our microscope, we use a condenser ZP lens with an overall diameter of 1 cm and an outer zone width of 50 nm. The high-resolution objective ZP lens has a diameter of 63 μm, 618 zones, a focal length of 650 μm at 2.4 nm wavelength, and an outer zone width of 50 nm.

Because SXT is fast (~ 5 min per tomographic data set), we can examine large numbers of cells. Since organic material absorbs approximately an order of magnitude more strongly than water, a unique and quantifiable natural contrast image of cellular structures is generated. X-ray absorption follows Beer's Law, therefore the absorption of photons is linear and a function of the biochemical composition at each point in the cell. As a result, a linear absorption coefficient (LAC) value of each voxel can be calculated. For example, lipid drops with high concentrations of carbon are more highly absorbing (LAC=0.7 mm^{-1}) than fluid-filled vesicles (LAC=0.2 mm^{-1}). We can determine the position of specific molecules by overlaying fluorescence microscopy signals on cell structures obtained with x-ray imaging. In addition, we can directly determine the locations and numbers of metal probes throughout the cell.

9:20am **NL+AS+BI+SA-FrM4 Ultrathin Electron Transparent Membranes as a Platform for Scanning Electron and Photoelectron Imaging and Spectroscopy of Fully Hydrated Nanoparticles**, ***X.M. Ma***, *J. Geisler-Lee*, Southern Illinois University Carbondale, *M. Amati, L. Gregoratti*, Sincrotrone Trieste, Italy, *S. Guenther*, Technical University Muenchen, Germany, *M. Kiskinova*, Sincrotrone Trieste, Italy, *A. Kolmakov*, Southern Illinois University Carbondale

The increased use of engineered nanoparticles (ENPs) in biomedical applications and their inevitable release into the environment has prompted considerable need to study of their uptake, accumulation and transport inside biological tissue and in plants. This is particularly true for addressing the ENPs fate on a cellular level which inevitably requires the microscopy approach. For long time optical microscopy with the resolution in the order of 100 nm was the major tool available. Better resolution can be readily achieved with traditional transmission (TEM) or scanning (SEM) electron microscopy. However, it requires histological sample treatments such as fixation, staining, dehydration, freezing etc which excludes *in vivo (in situ)* modes of observations and can alter their native morphology, functionality and living cycles. Different from standard environmental SEM, where the near sample pressure is limited by ca few tens of Torr, we are actively working on fabrication and tests of electron transparent membranes for ambient pressure electron spectromicroscopy and its application to fully hydrated samples for phytotoxicity, and materials research. Such enclosed environmental cells, equipped with 50-100 nm windows transparent for 10-20 keV electrons, can maintain the sample at atmospheric pressure and/or fully hydrated. This approach is beneficial compared with dry methods since *in vivo* SEM/TEM observations at nanoscale can be performed. Using this methodology, we were able to image the uptake of silver (Ag) NPs by living Arabidopsis roots on a cellular level. It was shown that NPs with the sizes larger than 20 nm accumulate preferably on the surface of the cellular walls and do not to traverse the plant cell membrane.

Recent developments in high yield fabrication and handling protocols of ultrathin (~1 nm) membranes, such as graphene or graphene oxide sheets with thicknesses comparable to the effective attenuation length (EAL) of 200-1000 eV electrons opened the opportunity to perform traditional XPS (X-ray Photoelectron Spectroscopy) and AES (Auger Electron Spectroscopy) at the interfaces between the membrane and fully hydrated samples. Using model water solutions and NPs, we report here on major design principles of such cells as well on first spectral demonstrations, advantages and limitations of this new technique.

9:40am **NL+AS+BI+SA-FrM5 Small-angle X-ray Scattering Investigation of Functional Materials at Inorganic-Marcromolecular Interfaces**, ***T.W. van Buuren***, *T.M. Willey, J.R.I. Lee, I.C. Tran, M. Bagge-Hansen*, Lawrence Livermore National Laboratory

Development in nanoscale engineering has enabled bioelectronics that can mimic and/or interact with the biological systems. Lipid bilayer-functionalized Si nanowires are considered as a promising candidate for the construction of bioelectrochemical devices. These biomimetic lipid bilayers serve as a general host matrix for bio-functional components such as membrane proteins. Though meaningful technological advancement of these materials has been made, critical questions about their structural and chemical composition remain. Small angle x-ray scattering (SAXS) experiments are used to investigate the structure of the lipid bilayers on Si nanowires, which provide information on the overall 1-D bilayer structure, the effect of substrate curvature on the lipid packing and local self-organization. The SAXS derived lateral-averaged characterizations are then corroborated with local arrangements of lipid bilayers on Si nanowires revealed by Scanning Transmission X-ray Spectroscopy (STXM). The results provide insights into a number of unresolved questions that are crucial for the comprehensive understanding this class of materials.

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