Biomaterial Interfaces
Room: 23 - Session BI-MoM

Surfaces to Control Cell Response
Moderator: A. Rosenhahn, Karlsruhe Institute of Technology, Germany

8:20am **BI-MoM1 Click Chemistry on Brominated Plasma Polymer Thin Films for Immobilizing and Patterning Biomolecules and Cells**, ***B.W. Muir***, CSIRO Materials Science and Engineering, Australia, *R. Chen,* CSIRO Materials Science and Engineering and The University of Melbourne, Australia, *G.K. Such,* The University of Melbourne, Australia, *A. Postma, R.A. Evans, K.M. McLean,* CSIRO Materials Science and Engineering, Australia, *F. Caruso*, The University of Melbourne, Australia

The development of versatile and robust strategies for the surface modification of multiple classes of materials has proven challenging, with few generalized methods. Many available methods have limitation for widespread use due to the need for specific surface chemistries and/or laborious multistep procedures[1]. A protocol to deposit brominated plasma polymer (Brpp) thin films on a variety of substrate surfaces (silicon wafers, glass, gold, Teflon) has been developed. These coatings are highly adherent and exhibit good stability in aqueous, biphasic and autoclaving conditions. The Brpp coating was found to be a useful platform for secondary reactions leading to surfaces with specific chemical properties. Following nucleophilic exchange, azide functionalized surfaces were developed and the copper catalysed azide alkyne cycloaddition (CuAAC) reaction[2]; a paradigm of click chemistry, was successful in immobilizing various acetylenes. A particular highlight is the patterning of cells via selective surface functionalisation of PEG-alkyne using a photomask.[3] This is the first known example of CuAAC reactions on pp thin films. A detailed physicochemical characterisation study of these films will also be presented.

[1] aH. Lee, S. M. Dellatore, W. M. Miller, P. B. Messersmith, *Science* 2007, 318, 426-430; bD. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, T. P. Russell, Science 2005, 308, 236-239.

[2] R. A. Evans, *Australian Journal of Chemistry* 2007, 60, 384-395.

[3] Chen, R. T.; Marchesan, S.; Evans, R. A.; Styan, K. E.; Such, G. K.; Postma, A.; McLean, K. M.; Muir, B. W*.; Caruso, F., *Biomacromolecules* 2012, 13, (3), 889-895.

8:40am **BI-MoM2 Temperature-Induced Electrostatic Assembly of Poly (Ethylene Glycol) Co-Polymer for Non-Fouling Biomedical Applications: How Low Can You Go?**, ***R. Ogaki***, *O. Zoffmann Andersen, K. Kolind, D.C.E. Kraft, M. Foss*, Aarhus University, Denmark

Development of long-term stable surfaces that resist bio-adhesion continues to stimulate the field of biomedical and biological research. While numerous strategies have been developed over the last several decades, the challenge remains in the creation of surfaces that can provide long-term 'zero' bio-adhesion from a variety of biological entities that spans lengths scales from biomolecules to cells. Although the physical and chemical properties of the resisting surface itself are important in achieving this ultimate goal, assessing the extent of bio-adhesion must be accompanied by detailed surface analysis via highly sensitive analytical techniques.

We have recently discovered that increasing the temperature alone during the assembly process of poly-*l*-lysine *grafted* poly (ethylene glycol) (PLL-*g*-PEG) results in the formation of highly dense PLL-*g*-PEG brush coating. The PLL-*g*-PEG surfaces prepared at various temperatures (20 to 80 °C) have been characterized by X-ray photoelectron spectroscopy (XPS). The PLL-g-PEG surfaces prepared at the 'standard' temperature of 20 °C are found to be comparable to the previously reported literatures. Interestingly, the surfaces prepared at 80°C have shown the highest surface grafted density of PLL-*g*-PEG, with ~ 4 times denser than those prepared at 20 °C.

The degree of cell and protein adhesions on these surfaces has been stringently determined using cell culture and serum/blood adsorption assays combined with XPS and time of flight secondary ion mass spectrometry (ToF-SIMS). The temperature-induced PLL-*g*-PEG surfaces have achieved 'zero' cell adhesions from three different types of mammalian cells for at least 36 days. In addition, XPS and ToF-SIMS analysis have confirmed near-zero protein adsorptions from 10% serum/MEM (at least 36 days), whole undiluted blood (at least 24 hrs) and undiluted serum (at least 24 hrs) with the surfaces being pre-incubated in high ionic strength buffer (2.4 M NaCl for 24 hrs).

The outcome of the rigorous bio-resistance tests presented here highlights the critical importance of processing temperature on the surface graft density of electrostatically driven PLL-g-PEG. The temperature induced assembly process can be effectively and easily implemented for a range of biomedical and biotechnological applications.

9:00am **BI-MoM3 Spatially and Temporally Coordinated Processes of Cells at Molecular to Cellular Scales**, ***J.P. Spatz***, Max Planck Institute for Intelligent Systems & University of Heidelberg, Germany **INVITED**

Our approach to engineer cellular environments is based on self-organizing spatial positioning of single signaling molecules attached to synthetic extracellular matrices, which offers the highest spatial resolution with respect to the position of single signaling molecules. This approach allows tuning tissue with respect to its most relevant properties, i.e., viscoelasticity, peptide composition, nanotopography and spatial nanopatterning of signaling molecule. Such materials are defined as "nano-digital materials" since they enable the counting of individual signaling molecules, separated by a biologically inert background. Within these materials, the regulation of cellular responses is based on a biologically inert background which does not initiate any cell activation, which is then patterned with specific signaling molecules such as peptide ligands in well defined nanoscopic geometries. This approach is very powerful, since it enables the testing of cellular responses to individual, specific signaling molecules and their spatial ordering. Detailed consideration is also given to the fact that protein clusters such as those found at focal adhesion sites represent, to a large extent, hierarchically-organized cooperativity among various proteins. We found that integrin cluster have a functional packing density which is defined by an integrin-integrin spacing of approximately 68 nanometers. Such critical spacing values vary as matter of transmembrane receptor choice of interest. We have also developed methods which allows the light initiated activation of adhesion processes by switching the chemical composition of the extracellular matrix. This enabled us to identify the frequency of leader cell formation in collective cell migration as a matter of initial cell cluster pattern size and geometry. Moreover, "nano-digital supports" such as those described herein are clearly capable of involvement in such dynamic cellular processes as protein ordering at the cell's periphery which in turn leads to programming cell responses.

9:40am **BI-MoM5 Chemically Defined Synthetic Surfaces for Mesenchymal Stem Cell Expansion**, ***L. Meagher***, *H. Thissen, P. Pasic, R.A. Evans, S. Pereira, K. Tsang, V. Glattauer, K. Styan, C.L. Be, D. Haylock*, CSIRO Materials Science and Engineering, Australia

Interest in surface initiated polymerisation (SIP) for biomedical applications has increased rapidly recently, particularly the use of "living" free radical polymerisation mechanisms[1] as highly defined coating properties/architectures can be achieved. Here we demonstrate that advanced coatings can be produced using a surface immobilised macro-chain transfer agent approach[2] and that such coatings can be used for the effective control of cell-surface interactions, an essential requirement in a broad range of applications in biomaterials and regenerative medicine. In the expansion of stem cells for therapeutic applications, fully synthetic, chemically defined materials are a requirement. Polymeric coatings which contain synthetic cell signalling molecules are key to ongoing progress in the generation of cells as therapies. Coating characterization was carried out using X-ray photoelectron spectroscopy (XPS) and colloid probe atomic force microscope (AFM). Cell culture studies were carried out using bone marrow derived human mesenchymal stem cells (hMSCs) using standard techniques. Differentiation of hMSCs was carried out using standard protocols in induction medias and the presence of characteristic cell surface markers was determined using flow cytometry. Substrate materials were silicon wafers or tissue culture polystyrene (TCPS).

In this study, we focus on a surface initiated Radical Addition-Fragmentation chain Transfer (RAFT) approach and present data demonstrating that dense polymer brushes can be prepared via surface immobilized macro-RAFT agents. The brush nature of the coatings was confirmed using a combination of XPS analysis and direct interaction force measurements with the AFM colloid probe technique. The properties of the coatings could be fine tuned using a variety of parameters such as the RAFT agent surface density, the polymerisation conditions, the monomer feed composition and the conjugation of cell attachment motifs such as cyclic peptides which interact with cell surface integrins. For example, the combination of a low cell adherent, low protein adsorbing polymer brush coating containing a conjugated peptide which interacted with $alpha_v beta_3$ integrins resulted in a surface which supported the expansion of hMSCs in a xeno-free, chemically defined, serum replacement media. In addition the expanded cells expressed cell surface markers typical of undifferentiated

hMSCs and the expanded cells were able to differentiate along adipogenic, osteogenic and chondrogenic pathways.

[1] Edmond, S., Osborne, V.L. and Huck, W.T.S., Chem. Soc. Rev. 2004, 33, 14.[2] Meagher, L., Thissen, H., Pasic, P., Evans, R.A. and Johnson, G., WO2008/019450.

10:00am **BI-MoM6 Binary Colloidal Crystal Structures Combined with Chemical Surface Modification to Achieve Superior Control Over Biointerfacial Interactions**, ***P. Koegler***, Swinburne Univ. of Tech., Australia, *P. Pasic, J. Gardiner, V. Glattauer,* CSIRO Materials Science and Eng., Australia, *A. Clayton,* Swinburne Univ. of Tech., Australia, *H. Thissen,* CSIRO Materials Science and Eng., Australia, *P. Kingshott*, Swinburne Univ. of Tech., Australia

Biointerfacial interactions play a major role in the field of biomedical materials and regenerative medicine and are of tremendous importance to *in vivo* and *in vitro* applications. Cell-material interactions are mediated by surface parameters including the materials surface chemistry and topography. Colloidal lithography represents a promising tool to modify surface topographies at the nanoscale with precision and over large areas while at the same time not requiring complex instrumental set-ups or rigorous experimental conditions. The creation of nanostructured surfaces in this way can also be combined with sophisticated surface modification techniques such as polymer grafting techniques via functional groups (grafting-to) or initiating groups (grafting-from) on the particle surface. This platform, which provides control over surface chemistry and topography, offers great flexibility in regard to the design of advanced surface coatings.In the current study we have generated highly ordered binary colloidal crystal structures using surface functionalized particles. This approach allows precise control over particle size, spacing, and thus pattern morphology. In order to minimize undesired non-specific protein adsorption which can mediate cell attachment, graft polymer coatings were applied to particles using heterobifunctional poly(ethylene glycol) (PEG) to render the surfaces non-fouling. In addition, colloid crystal modified surfaces were modified with specific bioactive signals, such as the cyclic RGD peptide (cRGDfK) to promote cell attachment. Surface characterization was carried using scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS). Cell culture experiments were carried out using L929 mouse fibroblasts up to 24 hours.The unprecedented control over the surface chemistry and topography provided by this simple coating platform is of significant interest for the study of biointerfacial interactions and the development of new and improved biomedical devices.

11:20am **BI-MoM10 Influence of Ca^{2+} Binding to Titania on Platelet Activation Profiles**, *S. Gupta,* ***I. Reviakine***, CIC biomaGUNE, Spain

Surface properties of implant materials are known to influence biological responses they elicit. However, complex processes operating at the interface remain poorly understood. To get an insight into these processes, we investigated the role played by surface ion equilibrium in defining interactions between an implant material (TiO_2) and components of blood (in this case, platelets), because blood is the first tissue that foreign materials come into contact with when inserted into the body and because platelet response is crucial in defining the implant's fate.

Titanium is a widely used biomaterial. Its success is in part due the favorable biocompatibility properties conferred by its oxide, TiO_2. We have previously shown that Ca^{2+}-TiO_2 interactions affect the distribution of phospholipid phosphatidyl serine (PS) in model lipid membranes prepared on TiO_2. This allowed us to hypothesize that platelet activation will be affected by these interactions as well.

Platelets are anuclear cell fragments circulating in blood. Activated at wound sites, they aggregate and provide a catalytic surface for the formation of a fibrin-based clot that stops the bleeding. Recently, platelets have been recognized to participate in inflammation, wound healing, tissue regeneration, and immune responses. Activation of platelets by foreign surfaces is detrimental to blood-contacting implants but beneficial for osteoimplants. Upon activation, platelets expose on their surface and secrete a number of markers. These include PS, activated form of GPIIb-IIIa, and proteins CD62P and CD63 that are found in the membranes of the intracellular α- and dense granules of quiescent platelets. To assess the state of platelet activation on TiO_2, we assayed for the expression of these markers. In order to isolate a clear cause-and-effect relationship between Ca^{2+}-TiO_2 interactions and platelet activation, we focused on purified platelets.

Our main finding is that the platelet activation profile on TiO_2 depends on the presence of Ca^{2+}. Furthermore, in the absence of Ca^{2+}, the α- and dense granule secretion is differentially regulated on titania. The differential granule secretion by platelets, as regulated by the surface properties, can be applied towards controlled release of molecules from platelets by nanoparticles or implants in drug delivery applications.

11:40am **BI-MoM11 Enhancing the Osseointegration of Titanium Dental Implants by Magnetron-Sputtered Strontium Containing Coatings**, ***O.Z. Andersen***, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark, *V. Offermanns,* Medizinische Universität Innsbruck, Universitätsklinik für Mund-, Kiefer- und Gesichtschirurgie, Austria, *M. Sillassen,* Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark, *D.C.E. Kraft,* Aarhus School of Dentistry, Denmark, *J. Bøttiger, F. Besenbacher,* Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark, *F. Kloss,* Medizinische Universität Innsbruck, Universitätsklinik für Mund-, Kiefer- und Gesichtschirurgie, Austria, *M. Foss*, Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark

Introduction: Strontium (Sr) has been shown to have a beneficial influence on the subsequent remodelling of the bone structure in relation with implant osseointegration. Both decrease of the osteoclast driven bone resorption and enhancement of the osteoblast driven process of bone formation has been shown. Furthermore, Sr has proven to have an anti-inflammatory effect.

Methods: The coatings used in this study were either prepared on Ti implants (rods with diameter = 1.1 mm and length = 6 mm) or on silicon wafers. The Sr containing surface modifications were prepared by co-sputtering in a setup with a pure Ti and a sintered composite target. The samples were characterized using SEM, AFM, XPS and RBS. ICP-AES was used to investigate the amount of Sr released from the samples as a function of time. Human dental pulp stem cell (hDPSC) cultures were used to assess the *in vitro* cellular response: Cell attachment and proliferation was studied along with the cells ability to mineralize. Quantification of osteogenic expression markers and specific cytokines was performed via RT-PCR. Human blood derived monocyte cultures were carried out to investigate the *in vitro* differentiation of these into osteoclast-like cells in response to Sr. *In vivo* experiments were carried by inserting implants into the femur of Wistar rats and evaluation was done by assessing bone-to-implant contact and new bone volume.

Results: The amount of Sr incorporated in the surfaces was found to be between 0 and 8.7 at. %. The Sr release profile showed that the most Sr was released from samples incorporating 5.5 at. % Sr. In relation with the *in vitro*experiments, the hDPSC proliferation and mineralization was found to correlate with the surface Sr concentrations. Moreover, the Sr concentration also affected the differentiation of monocytes into osteoclast-like cells. In relation with the *in vivo* experiment it was found that the incorporation of Sr had a beneficial effect on implant osseointegration, where an increase in direct bone contact and in new bone volume was observed with an increasing Sr release.

Discussion: From the *in vitro* and *in vivo* Sr release experiments it was found that a more dense surface structure developed as the Sr concentration were increased. We therefore speculate that the peak in the Sr release around 5.5 at.% can be ascribed to an optimal correlation between the morphology and the amount of incorporated Sr. The results from the *in vitro* and *in vivo* models shows that the coating process we have developed for modifying implants is an interesting candidate in relation with shortening the healing period when inserting osseointegrating implants.

Biomaterial Interfaces
Room: 23 - Session BI-MoA

Cell-Surface Interactions: High Throughput Methodologies

Moderator: M.R. Alexander, University of Nottingham, UK

2:00pm **BI-MoA1 3D Niche Microarrays for Systems-Level Analyses of Stem Cell Fate**, *A. Ranga,* ***M. Lutolf***, École Polytechnique Fédérale de Lausanne, Switzerland **INVITED**

Proper tissue maintenance and regeneration relies on intricate spatial and temporal control of biochemical and biophysical microenvironmental (or 'niche') cues, instructing stem cells to acquire particular fates, for example remaining quiescent or undergoing self-renewal divisions. Despite rapid progress in the identification of relevant niche proteins and signaling pathways using powerful *in vivo* models, many stem cell types cannot be efficiently cultured *in vitro*. To address this challenge, we have been developing b iomaterial-based approaches to display stem cell regulatory signals in a precise and near-physiological fashion, serving as powerful artificial microenvironments to probe and manipulate stem cell fate. In this talk I will discuss recent efforts in my laboratory to develop three-dimensional microarrayed artificial niches based on a combination of biomolecular hydrogel engineering and liquid handling robotics. This platform allows key biochemical and biophysical characteristics of stem cell niches to be mimicked and the physiological complexity deconstructed into a smaller, experimentally amenable number of distinct signaling interactions. The systematic deconstruction of a stem cell niche may serve as a broadly applicable paradigm for defining and reconstructing artificial niches to accelerate the transition of stem cell biology to the clinic.

2:40pm **BI-MoA3 Microfluidic Gradient Systems to Generate Defined Cell Microenvironments and Study Cellular Fate Processes**, *P. Wallin, E. Bernson,* ***J. Gold***, Chalmers University of Technology, Sweden

Cell microenvironments are the main driving force in cellular fateprocesses and phenotype expression in vivo. In order to mimic specific stem cell niches, and study cellular responses under those conditions in detail, we need the ability to create and control cell micro environments in vitro. This includes the capability to modify growth substrate surface properties, liquid composition as well as cell-cell interactions in cell culture systems. Microfluidic systems offer the possibility to modify liquid mixtures on the cellular length scale in a highly defined manner. In particular, the ability to generate spatially- and temporally- controlled liquid gradients is of high relevance to study concentration dependent cell responses.

We are using a diffusion-based gradient generator that has been characterized both by computational fluid dynamic simulations, as well as experimentally. Themicro fluidic network was used to investigate HUVEC endothelial cell migration along chemotractant VEGF gradients when simultaneously grown on a continuous gradient in spacing of cell attachment peptide (cRGD) via functionalized Aunanoparticles (65-85nm spacing over 6 mm). The aim of this study is to ascertain how cell migration is affected by the spacing of attachment peptides. This has been achieved by forcing cells to migrate in a chemotrative gradient on a gradient substrate which will have portions that do not support mature focal adhesion formation or cell spreading. The same microfluidic network was also used in combination with a micro grooved growth substrate to study myoblast differentiation and alignment in response to simultaneous chemical (specifically, gradients in media composition) and topographical stimulation. This was performed in order to define the growth media and to optimize its composition.

The developed platform allows monitoring phenotype expression of cells in situ in highly controlled gradient environments of soluble factors in combination with different cell culture substrate properties. The detailed investigation of specific cellular responses to those stimuli is very difficult and timeconsuming with standard cell culture techniques.

The research leading to these results has received funding from the EU 7th Framework Programme (FP7/2007---2013) under grant agreement NMP3---SL---2009---229294 NanoCARD, and from Vinnova under contract no: 2009---00227.

3:00pm **BI-MoA4 What Makes the Heart Grow Fonder? High Throughput Screening of Synthetic Surfaces for Cardiomyocyte Culture**, ***A.K. Patel***, *M.R. Alexander, M.C. Davies,* University of Nottingham, UK, *D.G. Anderson, R. Langer,* Massachusetts Institute of Technology, *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 targets[1]. The maturation and maintenance of the cardiomyocyte phenotype may be controlled by the manipulation of the substrate supporting the cells[2]. 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 approach[3] 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 spectrometry[4].

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.

References:

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

4:20pm **BI-MoA8 High-throughput Discovery of Polymers for Stem Cell Culture**, ***A.D. Celiz***, Univeristy of Nottingham, UK, *M. Mahlstedt, A.L. Hook, D.J. Scurr,* University of Nottingham, UK, *D.G. Anderson, R. Langer,* Massachusetts Institute of Technology, *D.A. Barrett, C. Denning, L. Young, M.C. Davies, M.R. Alexander*, University of Nottingham, UK

Numerous regenerative medicine procedures are already in clinical trials or in the pipeline and if these succeed and reach the clinic, stem cell factories will be needed to meet demand for the billions of cells required per intervention. Current protocols for stem cell culture employ poorly defined biological substrates such as Matrigel™, and/or non-human feeder cell layers which exhibit batch-to-batch variability, and are a potential source of pathogens. More recently, recombinant protein surfaces have been successfully employed, but these are not always cost effective for high-throughput culture methods. Consequently, there is significant research into xeno-free culture alternatives that use fully defined culture media and synthetic substrates. To discover materials for application as substrates, we have used high-throughput polymer arrays with which to fabricate chemically defined and scalable stem cell culture systems. A combinatorial chemical polymer library can be synthesized as a microarray on-slide allowing cell response of hundreds of different materials on a single glass slide, enabling hit materials to be identified in an automated manner [1]. High-throughput surface characterization (HT-SC) can be performed on the polymer microarray to (i) rapidly evaluate the surface chemistry of each individual spot and (ii) identify surface structure-property relationships in the complex and large datasets generated. (2)

In this study, a polymer library substantially increased in number and diversity compared with previous studies is prepared by printing (meth)acrylate monomers in pair-wise combination on a polyHEMA coated slide. HT-SC is carried out using time-of-flight secondary-ion mass

spectrometry, X-ray photoelectron spectroscopy, atomic force microscopy and water contact angle to characterize all polymer surfaces. Human pluripotent stem cell (hPSC) attachment is probed using automated fluorescence microcopy. This suite of HT-SC techniques has allowed the identification of 'hit' materials that support the expansion and proliferation of hPSCs. Human embryonic stem cell lines (HUES7 and H9) are screened for attachment in 3 different media; mouse embryonic fibroblast-conditioned media (MEF-CM), StemPro® and mTeSR®1 without any protein preconditioning to provide an insight into the impact of material surface properties on cellular interactions. The hits identified represent novel platforms for hPSCs culture without the need for any protein preconditioning and show great potential for development into future synthetic culture systems.

[1] Anderson, D. G. *et al. Nat. Biotechnol.* **22**, 863 - 866 (2004).

[2] Mei, Y. *et al*. *Nat. Mater.* **9**, 768 – 778 (2010).

4:40pm **BI-MoA9 Plasma Polymer Films at the Interface: Biomaterial Applications**, ***B.R. Coad***, University of South Australia

Biomaterial research is primarily concerned with mediating the interaction of biological species at the surface of materials. Therefore, research into new ways of coating and derivatizing surfaces is advancing this field. Coating surfaces with thin plasma polymer layers is advantageous because fragmentation and recombination of organic compounds in the plasma phase allows for surface deposition leading to covalent anchoring of polymer networks that retain the functionality of the parent compounds. This is useful as a platform strategy, providing a substrate-independent path for modifying different classes of bulk materials so that they retain their bulk properties (hardness, softness, conductivity, inertness etc.).

In this presentation, we show how deposited plasma polymers form interlayers that allow further surface modification of 1) surface chemistry and 2) surface topology and relate these to their use as biomaterials.

In the first approach, we have constructed a bioconjugation platform that allows for covalent capture of proteins in a gradient fashion. Simultaneous gradient plasma polymerization of two compounds under a mask along a moving stage allows for an increasing surface density of reactive aldehyde groups to be place alongside an inert hydrophilic spacer allowing for specific, yet variable attachment to be mediated across the surface. We have used this platform to capture streptavidin on the surface to which we have bound biotinylated signaling probes to investigate T-Cell binding and specificity. This platform is shown to be useful in further immunological studies investigating T-Cell binding to gradients of assembled human major histocompatibility complex analogs.

In the second approach, the surface topology has been modified with polymer brushes. With controlled radical polymerization from a novel macroinitiator, it is possible to generate polymer brushes of variable thickness and density which in turn modify the surface interaction with proteins and cells. Polymer chains which are present in highly ordered array provide an entropic barrier to surface fouling and cell attachment. The advantage of using plasma polymer interlayers is that the substrate-independent procedure allows for coatings with the same topology to be grafted, for example, from the surface of a hard, inert metal or from a flexible, polymeric film.

We conclude by showing a few other examples of the use of plasma polymerization for biomaterials applications from our latest work.

5:00pm **BI-MoA10 A High Throughput Strategy for Studying Protein Pre-adsorption to Materials Developed for Stem Cell Culture**, ***M. Hammad***, University of Nottingham, UK, *D.G. Anderson, R. Langer,* Massachusetts Institute of Technology, *M.R. Alexander, M.C. Davies*, University of Nottingham, UK

Improved biomaterials are required for application in areas such as regenerative medicine, biosensors, and medical devices. The performance of such materials is often dependent on their surface properties which can influence factors such as cell attachment and *in-vivo* biocompatibility and assimilation. High throughput (HT) materials discovery techniques have been developed to gain a greater fundamental understanding of the nature of the cell-surface interaction[1]. We have developed polymer microarray systems using several hundred unique polymers synthesised rapidly on-slide enabling parallel assessment of cell-surface response[2]. HT materials discovery is thus possible when this platform is combined with HT surface characterisation derived structure activity relationships[3].

The response of cells to these materials is controlled by the identity and conformation of the proteins adsorbed to the surface, which is in turn controlled by the chemistry of the underlying substrate. The complex nature of protein adsorption and their diversity in typical culture conditions makes this a difficult process to follow in-situ. Flaim et al. illustrated how printing of extracellular matrix (ECM) proteins can be used to investigate their role in stem cell differentiation and adhesion on a hydrogel surface[4]. We use an adaption of this methodology to analyse proteins adsorbed to a range of polymer surfaces in the form of spots on the array using piezo dosed solutions of ECM proteins. We have achieved this on polymer microarray systems, illustrating the ability to control both the pre-adsorption and also surface protein composition. Surface chemical analysis techniques including X-ray photoelectron spectroscopy and secondary ion mass spectrometry are used to characterise the protein identity and distribution at the surface. Polymerisation was achieved using the deposition of monomer solutions by piezo dispensing nozzles in an array format onto pHEMA coated substrates before the slides were irradiated with a long wave UV source. ECM protein solutions were then printed on the polymer spots allowing cell response to be correlated with protein surface composition using the same apparatus.

1. Hook, A.L., et al. Biomaterials, 2010. (2): p. 187-198.

2. Anderson, D.G., S. Levenberg, and R. Langer Nature Biotechnology, 2004. (7): p. 863-866.

3. Mei, Y., et al Nature Materials, 2010. (9): p. 768-778.

4. Flaim, C.J., S. Chien, and S.N. Bhatia Nature Methods, 2005. (2): p. 119-125.

5:20pm **BI-MoA11 Combinatorial Development of Biomaterials for Pluripotent Human Stem Cell Culture**, ***Y. Mei***, Clemson University

Pluripotent human stem cells include human embryonic stem cells (hESCs) and more recently developed human induced pluripotent stem cells (hIPSCs). These cells can replicate indefinitely in culture and can differentiate into all types of cells in human body. Thus, they hold remarkable promise as cell source for regenerative medicine and tissue engineering applications. However, hESCs and hIPSCs are currently cultured on a feeder cell layer of mitotically inactivated mouse embryonic fibroblasts (mEFs) or Matrigel^{TM},extracellular matrix (ECM) protein mixtures secreted by mouse carcinoma cells. The utilization of mouse feeder cells and Matrigels as substrates leads to cell populations unsuitable for replacement therapy.

To address the challenge, we recently developed a high throughput polymer microarray technology to rapidly synthesize and test thousands of microscale substrates for hESC and hIPSC culture. In this study, 22 acrylate monomers were used to construct polymer arrays containing 496 different materials with diversified properties. Material properties including surface wettability, indentation elastic modulus, surface roughness and surface chemistry of each polymeric substrate in the array were quantified using high throughput methods. The results were then used to establish structure-function relationships between material properties and biological performance. Surface chemistry was shown to have controlling effects on hES cell undifferentiated growth while indentation elastic modulus or roughness had less pronounced effects on growth. The optimal ("hit") surface was defined as certain oxygen containing ions and hydrocarbon ions in time of flight secondary ion mass spectrometry [ToF-SIMS] analysis. The "hit" surfaces can effectively enhance adsorption of vitronectin and engagement with integrin a_vb_3 and a_vb_5 to promote self-renewal of hESCs and hIPSCs.

Based on the structure-function relationship, favorable substrates for hESC and hIPSC culture was developed by exposing polystyrene (PS), a typical cell culture plastic, to an optimized dose of short wavelength ultraviolet (UV) light. In this way, key chemical moieties supporting self-renewal of hESCs and hIPSCs (e.g. hydrocarbons and ester/carboxylic acid) can be introduced onto the surface of PS. PS surfaces treated with the optimal dose of UV (i.e. UVPS) can support more than three times more cells per area than traditional mouse embryonic fibroblast (mEF) feeder cells, the current gold standard. As "hit" polymers, UVPS can promote adsorption of vitronectin to support self-renewal of hESCs and hIPSCs.

Spectroscopic Ellipsometry Focus Topic
Room: 19 - Session EL+TF+BI+AS+EM+SS-MoA

Spectroscopic Ellipsometry: From Organic and Biological Systems to Inorganic Thin Films
Moderator: M.S. Wagner, The Procter & Gamble Company

2:00pm **EL+TF+BI+AS+EM+SS-MoA1 Biochemical Optical Sensors Based on Highly-Ordered Slanted Columnar Thin Films**, ***D. Schmidt***, *K.B. Rodenhausen,* University of Nebraska-Lincoln, *J. VanDerslice, T.E. Tiwald,* J.A. Woollam Co., Inc., *E. Schubert, M. Schubert*, University of Nebraska-Lincoln

Highly-ordered three-dimensional nanostructure thin films offer substantially increased surface area for attachment of organic layers, and in

addition, new detection principles due to the physical properties of the nanostructures. For example, upon material attachment the optical birefringence of the nanostructures changes due to screening of polarization charges. Because of these advantages, highly-ordered three-dimensional nanostructure thin films lend themselves as suitable candidates for studying of organic attachments as well as for low-cost humidity sensing, for example.

We utilize glancing angle electron-beam deposition for fabrication of highly spatially coherent metal slanted columnar thin films. Subsequently, the nanostructures may be further functionalized with thin conformal coatings by means of atomic layer deposition. The ellipsometry model analysis and resulting anisotropic optical properties of hybrid metal slanted columnar thin films determined by generalized spectroscopic ellipsometry in the visible and near-infrared spectral region will be discussed. We will be reviewing research in this area and report in particular on in-situ monitoring of organic attachments using ellipsometry combined with quartz crystal microbalance with dissipation. Exemplarily, we discuss studies of fibronectin protein adsorption, octanethiol chemisorption (self-assembled monolayer growth) on platinum coated titanium slanted columnar thin films as well as relative humidity sensing.

2:20pm **EL+TF+BI+AS+EM+SS-MoA2 Studies of Optical Properties of Hybrid J-aggregates and Nanocrystal Quantum Dots Layers for Photonic Applications**, ***K. Roodenko***, *H.M. Nguyen, L. Caillard, A. Radja, O. Seitz, Yu.N. Gartstein, A.V. Malko, Y.J. Chabal*, The University of Texas at Dallas

The integration of organic materials and inorganic nanocrystal quantum dots (NQDs) on the nanoscale offers the possibility of developing new photonic devices that utilize the concept of resonant energy transfer between an organic material and NQDs. Electromagnetic coupling that takes place between excitons—bound electron–hole pairs—at the interfaces of the hybrid composite can be utilized for light-emitting, photovoltaic and sensor applications.

As the key ingredients for the nanocomposite material system reported in this work are the J-aggregates (JA, dye self-assembled molecules) that have exceptional optical absorption due to their strong oscillator strength. NQDs on the other hand combine a variety of important properties, such as high quantum yields, excellent photo- and chemical stability, and size dependent, tunable absorption and emission. Excitation energy transfer in NQDs / J-aggregate hybrids is characterized by their strong excitonic transitions at room temperature with spectrally well-defined absorption and emission.

In order to understand the energy transfer mechanisms in such complex systems, optical properties of JA and NQDs/JA hybrid systems were characterized by means of spectroscopic ellipsometry and polarized IR spectroscopy.

Spectroscopic ellipsometry in 0.6-5 eV spectral range was employed to study optical properties of J-aggregates drop-casted on silicon surfaces. Thin JA films were found to exhibit strong optical anisotropy due to the specific molecular orientation of thin layers on Si substrates. Variation of optical properties due to the deposition of nanocrystal quantum dots (NQDs) was systematically studied for applications in new photonic devices that utilize excitonic energy transfer from NQDs to JA layer. Ellipsometric results were cross-referenced with atomic force microscopy (AFM) data to derive a quantitative understanding of the distribution of NQDs upon deposition on JA layer. Integration of hybrid colloidal NQD/JA structures could be potentially attractive for a range of optoelectronic applications.

2:40pm **EL+TF+BI+AS+EM+SS-MoA3 Love and Death, the Story of Most Proteins and Most Surfaces as Told by Spectroscopic Ellipsometry**, *T. Benavidez, K. Chumbuni-Torres, J.L. Felhofer,* ***C.D. Garcia***, The University of Texas at San Antonio **INVITED**

Biosensors are analytical platforms that integrate a biological recognition element with a signal transducer. Because they have the potential to provide rapid, real-time, and accurate results, biosensors have become powerful tools in clinical and biochemical settings. Our group is particularly interested in the development of electrochemical biosensors based on enzymes adsorbed to nanomaterials. When integrated to microfluidic devices, these sensors offer sensitivity, portability, low cost, and the possibility of analyzing turbid samples. Adsorption was selected to immobilize the biorecognition element because it is one of the simplest and most benign methods, avoiding cross-linking reactions or additional components (such as entrapping polymers). Most importantly, as adsorption is a required (and sometimes limiting) step for any immobilization mechanism, the identification of key variables influencing this process can be applied to a variety of strategies. Although several techniques have been used to study the adsorption of proteins to nanomaterials,[1] only a few of them provide information about the kinetics of the process in real time. This is a critical aspect, as most of the post-adsorption conformational changes occur within a few minutes after the interaction.[2] Among those, reflectometry was used by our group to perform the first kinetic study related to the interaction of proteins with carbon nanotubes.[3] These kinetic studies have been recently extended to the interaction of enzymes (D-amino acid oxidase,[4] catalase,[5] and glucose oxidase[6]) by variable angle spectroscopic ellipsometry, which enabled a more thorough analysis of the interaction process with a much more versatile experimental design.[7,8] The use of VASE demonstrated that a number of variables, (being the amount of enzyme only one of them) can influence the biological activity of proteins adsorbed to the substrate. Furthermore, our results indicate that that the activity of enzymes adsorbed to nanomaterials can be directly related to the kinetics of the adsorption process (dG/dt).[5]

Please see supplemental document for figures and footnotes.

3:40pm **EL+TF+BI+AS+EM+SS-MoA6 Detailed Photoresist and Photoresist Processing Studies using Spectroscopic Ellipsometry**, ***C. Henderson***, Georgia Institute of Technology **INVITED**

Spectroscopic ellipsometry has become an invaluable tool for the study of a wide variety of thin film systems. In particular, it has become extremely valuable in the development and study of advanced photoresists and of lithographic processes used in the production of integrated circuits and other related semiconductor devices. In our work, we have used spectroscopic ellipsometry to study a variety of problems related to photoresists including swelling phenomena, exposure induced refractive index changes, and ultra-fast dissolution phenomena. We have combined spectroscopic ellipsometry with quartz crystal microbalance techniques to simultaneously study thin film optical properties, thickness, film mass, and film modulus. Such techniques have been particularly useful in understanding the dissolution properties of polymeric photoresists developed for 193 nm lithography. This talk will review some of the applications for spectroscopic ellipsometry in this field and in particular will highlight some of the results of our work made possible using spectroscopic ellipsometry.

4:20pm **EL+TF+BI+AS+EM+SS-MoA8 Ellipsometric Characterization of a Thin Titaniumoxide Nanosheets Layer**, ***H. Wormeester***, *G. Maidecchi, S. Kumar, A. Kumar, A. ten Elshof, H.J.W. Zandvliet*, MESA+ Institute for Nanotechnology, University of Twente, The Netherlands

The photochemical properties of titaniumoxide make this a widely studied material. Of special interest is a thin nanostructured layer of such a material. A variety of a nanostructured material is the single sheet titaniumoxide that can be obtained by delaminating a layered titanate, with stochiometry $Ti_{1-x}O_2^{-4x}$ (x=0.0875). The slight titanium deficiency leads to a negatively charged nanosheet that can be used as a building block in a layer by layer assembled composite film [1]. In this work we used Langmuir Blodget to deposit succesive thin layers of nanosheets. The electronic properties of these layers were investigated with ellipsometry and Scanning Tunneling Microscopy (STM). The optical spectra show the well known absoprtion peak at 4.6 eV for titaniumoxide nanosheets. The optical spectra can be well modeled with a Cody-Lorentz dielectric function profile providing a bandgap of … eV, a value also found from STM IV spectroscopy. The Cody-Lorentz profile also indicates a slight below band gap light absorption by the nanosheet material.

[1] T. Sasaki, Y. Ebina, T. Tanaka, M. Harada, M. Watanabe and G. Decher, Chem. Mater. 2001, 13, 4661

4:40pm **EL+TF+BI+AS+EM+SS-MoA9 Preparation of Abrupt $LaAlO_3$ Surfaces Monitored by Spectroscopic Ellipsometry**, *C.M. Nelson, M. Spies, L.S. Abdallah,* ***S. Zollner***, *Y. Xu, H. Luo*, New Mexico State University

$LaAlO_3$ is a polar perovskite oxide, used as a single-crystal substrate in oxide epitaxy. It has created much interest for novel electronic applications, because a two-dimensional electron gas is formed at $LaAlO_3/SrTiO_3$ heterostructures. The purpose of our work is twofold: First, we are interested in an accurate determination of the complex refractive index of $LaAlO_3$ at room temperature. Second, we studied the impact of various cleaning methods on the abruptness of the $LaAlO_3$surface.

We obtained a commercial single-side polished $LaAlO_3$substrate with 2-inch diameter and a (100) pseudo-cubic surface orientation.The surface was polished with an rms roughness below 0.8 nm. We determined the ellipsometric angles ψ and Δ for $LaAlO_3$ at 300 K from 0.7 to 6.5 eV. For a bulk insulator with a clean smooth surface, the phase change Δ should be zero or π below the band gap. In practice, this never happens, because surfaces are covered with overlayers (adsorbed organic or water vapors). Surface roughness has a similar effect on the ellipsometric spectra as a surface overlayer. Even for an abrupt bulk/air interface, there is a thin (~0.5nm) transition region where the electron wave functions leak from the crystal into the ambient. For the as-received sample, the data were described with a Tauc-Lorentz model for $LaAlO_3$, plus 2.1 nm of surface layer

thickness (described as an effective medium with 50% density of the bulk). After ultrasonic cleaning in acetone, the overlayer thickness decreased to 1.8nm. Next, we mounted the wafer in a UHV cryostat, pumped down to below 10^{-8}Torr, and acquired an ellipsometric spectrum at 70°. The surface layer thickness was reduced to 1.2 nm, presumably because a part of the adsorbed surface layer (especially water) desorbed under vacuum.

So far, everything worked as expected, but here it gets interesting: We heated the sample to 700 K for about an hour to desorb the remaining surface overlayer. After cooling down to 300 K, we measured the ellipsometric angles again at 70° angle of incidence from 0.7 to 6.5 eV. The ellipsometric angle Δ at 2 eV was reduced to below 0.2°, consistent with a surface layer thickness of less than 1 Å, much less than the surface roughness specified by the supplier (8 Å).

In conclusion, a macroscopically smooth and clean $LaAlO_3$surface was prepared by ultrasonic cleaning of the wafer in acetone, followed by heating in UHV to 700 K. The resulting surface layer thickness was below 1 Å, as measured by spectroscopic ellipsometry. We will report Tauc Lorentz parameters. We will also describe the temperature dependence of the $LaAlO_3$dielectric function from 77 to 700 K. This work was supported by NSF (DMR-11104934).

5:00pm **EL+TF+BI+AS+EM+SS-MoA10 Determination of the Refractive Index of a Gold-Oxide Thin Film Using X-Ray Photoelectron Spectroscopy and Spectroscopic Ellipsometry**, ***K. Cook***, *G.S. Ferguson*, Lehigh University

A two-step procedure will be presented for measuring the complex refractive index of an electrochemically produced oxide film on a gold surface. In the first step, the composition and the thickness of the oxide film were determined using angle-resolved X-ray photoelectron spectroscopy. The experimental composition defined the system, thereby avoiding assumptions about the film stoichiometry that would otherwise be required. The value of thickness derived from these measurements was then used to calculate n and k from ellipsometric data collected across the visible spectrum (350 - 800 nm).

Plasma Science and Technology
Room: 24 - Session PS+BI-MoA

Applications of (Multiphase) Atmospheric Plasmas (including Medicine and Biological Applications)
Moderator: G.Y. Yeom, Sungkyunkwan University, Korea

2:00pm **PS+BI-MoA1 Plasmas in Saline Solution Sustained Using Bipolar Pulsed Power Source – Tailoring the Discharge Behavior Using the Negative Pulses**, ***H.W. Chang****, *C.C. Hsu*, National Taiwan University, Taiwan, Republic of China

Plasmas in saline solutions have been extensively studied due to their wide applications. In this work, plasmas ignited in saline solution were studied. The plasma system consisted of two electrodes immersed in 0.2 M NaCl saline solution. The electrode where the plasma was ignited was a 0.5 mm - diameter Pt wire covered by a glass tube to precisely define the area exposes to the solution. The grounding electrode was a bare platinum wire with the same diameter. Diagnostic tools used included voltage and current probes, an optical emission spectrometer, and a photomultiplier tube. We studied plasmas driven by a bipolar pulse power source using repetitive positive and negative voltage pulses with adjustable width and amplitude. We used the positive voltage pulses to ignite the plasma while using the negative voltage pulses to tailor the electrolytic gas formation amount. Conditions with the positive voltage pulse fixed at +600 V with an 80 μs duration, and the negative pulse varying from 0 to 80 V with the duration ranging from 0 to 20 ms were tested. By changing the duration of each voltage pulses, the bubble dynamics and the plasma behavior can be effectively controlled. By increasing the negative voltage pulse amplitude, we observed a decrease in the maximum currents before the ignition of the plasma from 1.75 to 1.0 A . The time required for plasma ignition upon the onset of the positive voltage pulse was reduced. The above observations can be well explained by the coverage of the electrode surface by electrolytic gas. Optical emission spectroscopy showed that I_H(656 nm)/I_{Na}(588 nm) ratio increases from zero to 0.0035 when the negative voltage pulse amplitude increases from 0 to 80 V. This clearly showed hydrogen, the electrolytic gas, content in the bubble increased with the increase in negative voltage pulse amplitude. This work was supported by National Science Council of Taiwan, the Republic of China (100-2628-E-002-012 and 101-3113-E-002-002).

2:20pm **PS+BI-MoA2 Low Temperature Plasma Deactivation of Endotoxic Biomolecules: The Effects on Lipid A**, ***T.-Y. Chung***, *J.-W. Chu, D.B. Graves,* University of California Berkeley*, E. Bartis, J. Seog, G.S. Oehrlein*, University of Maryland

Effective removal of infectious organisms and/or biomolecules from medical instruments is essential to prevent infections and disease transmission. Intricate modern instruments are difficult to clean via thermal sterilization since they are often heat sensitive. Furthermore, bacterial endotoxin and prion proteins are known to be particularly resistant to conventional sterilization procedures.[1, 2] Low-temperature plasma is a promising option for surface sterilization of bacteria and deactivation of harmful biomolecules, but mechanisms of endotoxic biomolecule deactivation are poorly understood.[3] Using a vacuum beam system, we study the effects of vacuum ultraviolet (VUV) radiation, oxygen and deuterium radicals on lipid A, the immune-stimulating region of lipopolysaccharide (LPS). The endotoxic activity of lipid A samples is monitored by measuring the secreted interleukin-1β (IL-1β) in human whole blood. The results obtained from *ex situ* transmission Fourier transform infrared (FTIR) spectroscopy, *in situ* quartz crystal microbalance (QCM), *in situ* residual gas analysis and *ex situ* electrospray ionization mass spectrometry (ESI-MS) show that VUV photons cause bulk modification to the penetration depth of photons, ~200 nm. On the other hand, radicals mainly cause chemical etching and modification near the surface of lipid A films. Although the radical-induced etch yield of lipid A is much lower than VUV-induced photolysis, secondary ion mass spectrometry (SIMS) and human whole blood-based assay demonstrate that O and D radicals alter the film surface, leading to significant reduction of film endotoxicity. Important structures governing the endotoxic activity of lipid A, e.g. the fatty acid chains and the phosphate groups, are greatly reduced after radical exposure. Qualitatively similar results are observed when LPS films are exposed to either H atoms or VUV photons in low-pressure plasma. The deactivation effects of low energy ions and atmospheric pressure air plasma on lipid A films will also be presented.

[1] K. L. Williams, ed., Endotoxins: Pyrogens, LAL Testing and Depyrogenation, Informa Healthcare USA, Inc., New York, 2007.

[2] W. A. Rutala and D. J. Weber, Infect. Control Hosp. Epidemiol. **31**, 107 (2010)

[3] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

2:40pm **PS+BI-MoA3 Nonthermal Bioplasma Sources and its Interactions to the Microbial, Fungal, Yeast and Living Cells**, ***E.H. Choi***, *Y. Kim, G.S. Cho, G. Kwon, B.K. Min, H. Uhm,* Kwangwoon University, Republic of Korea*, P. Suanpoot,* Maejo University Phrae Campus, Thailand*, G. Lee, R. Jung, B. Park*, Kwangwoon University, Republic of Korea **INVITED**

We have investigated the atmospheric pressure (AP) nonthermal bioplasma sources and their characteristics as well as their interactions with biological cells of microbial, fungal, yeast, and living cells. The electron temperature and plasma density are measured to be about 1.1 eV~ 1.5 eV and $(1\sim3)\times10^{12}$ cm^{-3} , respectively,for the direct plasma jet and dielectric barrier discharge (DBD) plasma under Ar gas flow. The densities for the reactive oxygen species (ROS) such as the hydroxyl radicals (OH), superoxide anions($O2^{*-}$), and nitric oxide (NO) have also been investigated in these AP direct plasma, respectively, inside the saline culture media by the ultraviolet optical absorption spectroscopy. Herein, we have investigated the basic interactions of these AP nonthermal bioplasma with the living organisms in morphological and biomolecular aspects. We found that the secondary electron emision coefficient of the biological surface has been drastically increased by atmospheric bioplasma, which indicates the biological surface to be oxidized especially by the hydroxyl (OH) radical species. In order to elucidate the basic mechanisms for the cell shrinking and apoptosis leading to a cell death by the nonthermal bioplasma, the cell membrane potential changes have been measured and investigated inside the culture media based on the ROS density as well as cell capacitances. It is also found that the molecular electron energy band structure in these biological cells have been modified and shifted toward the vacuum surface energy level by the AP nonthermal bioplasmas due to cell oxidation, mainly caused by OH radicals. We have also investigated the confocal Raman spectroscopy and circular dichroism as well as various biological assays to clarify these characteristics.

***** Coburn & Winters Student Award Finalist

3:40pm **PS+BI-MoA6 Deactivation of Lipopolysaccharide and Lipid A by Radicals Produced in Inductively Coupled Plasmas**, ***E. Bartis***, University of Maryland, *T.-Y. Chung, J.-W. Chu, D.B. Graves,* University of California Berkeley, *J. Seog, G.S. Oehrlein*, University of Maryland

Low temperature plasma (LTP) treatment of surfaces has been shown to degrade and sterilize bacteria as well as deactivate harmful biomolecules [1]. However, a major knowledge gap exists regarding which plasma species e.g. ions, VUV photons, and reactive radicals, 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 are notoriously difficult to remove from surfaces by traditional sterilization methods [2]. In this study, LPS- and lipid A-coated silicon substrates were exposed to low pressure plasma-generated Ar and H radicals isolated from an inductively coupled LTP source by employing a gap structure [3] to examine the effects of plasma composition on etch rates and chemical properties. Bioactivity of LPS was measured using an enzyme-linked immunosorbent assay (ELISA). Ar neutrals caused a 5% reduction in bioactivity whereas exposure to H radicals using the same plasma operating conditions caused a 25% reduction in bioactivity. Ellipsometric data shows that H radical-only exposures cause less than 2 nm of material removal, indicating that surface modification is the major cause of deactivation and that complete etching and removal is not necessary. These modifications can inhibit the binding of receptor molecules, whose binding depends on a variety of interactions such as hydrophobic and electrostatic interactions and lock-and-key mechanisms. After plasma processing, samples were characterized by vacuum transfer to x-ray photoelectron spectroscopy (XPS) to study the chemical changes occurring on the film surface. With XPS, we observed that plasma-generated H radicals produce a C-rich surface by effectively removing O, N, and P, the latter of which is from phosphate groups that contribute to the pyrogenicity. The C 1s spectra shows a clear loss of N-C=O and O-C=O groups. This loss leads to the removal of lipid A's aliphatic chains, which are responsible for its toxicity. Direct H2plasma treatments also remove O, but fast material removal causes an increase in N and P due to the exposed core and O-chain on LPS. Radical-only ELISA results will be compared to direct and VUV-only treatments where material removal is significantly greater. This result is especially true for direct Ar plasmas, where modification/etching is dominated by ion bombardment. Our results compare favorably with complementary VUV/radical beam studies of lipid A.

[1] A. von Keudell et al., Plasma Process. Polym. **7**, 327 (2010)

[2] E. T. Rietschel et al., FASEB J. **8**, 217 (1994)

[3] L. Zheng et al., J. Vac. Sci. Technol. A **23**, 634 (2010)

4:00pm **PS+BI-MoA7 Localised, Non-Contact Surface Modification with Microplasma for Biotechnological Applications**, ***S.A. Al-Bataineh***, *E.J. Szili, D.A. Steele, N.H. Voelcker, H.J. Griesser, R.D. Short*, University of South Australia

Localised surface modification of "open" surfaces is important for many biotechnological applications. In this study, we describe the utilisation of microcavity plasma arrays for localised surface modification of materials in a non-contact approach. In contrast to the current methods for localised surface modification, our method achieves spatially controlled surface modification without the use of a physical mask, photolithography or contacting the surface. Therefore, it provides the opportunity to reduce the number of modification steps and thus the cost of surface engineering processes. To this end, a 7 x 7 microcavity plasma array device (each cavity is separated by 500 µm and has a diameter of 250 µm with a depth of 55 nm) was manufactured and operated in helium at atmospheric pressure to generate, under optimised operating parameters, spatially separated modified regions on passivated surface coatings. The microplasma-patterned coatings were then used to control the spatial distribution of biomolecules such as proteins by allowing protein adsorption onto the modified regions whereas the rest of the coating remains non-fouling. Therefore, this approach resulted in spatially separated areas of immobilised protein. These surfaces were also used to control the spatial distribution of other biomolecules as well as living cells.

4:20pm **PS+BI-MoA8 Biocompatible Nanocomposites Synthesized by Gas-Liquid Phases Plasmas**, ***T. Kaneko***, *Q. Chen, R. Hatakeyama*, Tohoku University, Japan **INVITED**

Recently, multiphase plasmas, particularly gas-liquid phases plasmas have attracted much attention as fundamental and application researches [1], because the non-equilibrium plasmas in gas phase can produce the various kinds of chemically active ions and radicals which react with nano- and bio-materials stably existing in liquid. As one of the promising applications of the gas-liquid interfacial discharge plasmas (GLIDPs), the synthesis of various kinds of nanoparticles [2] is advantageous in that toxic reducing agents are unnecessary and the synthesis is continuous during the plasma irradiation. In addition, the GLIDPs are also used in the biomedical field, for example, the synthesis of gold nanoparticles (AuNPs) conjugated with biomolecules such as DNA. The DNA conjugated AuNPs (DNA-AuNPs) work as vectors to deliver DNA into living cells because the AuNPs can be efficiently manipulated by a light field. Furthermore, the DNA-AuNPs are attempted to be encapsulated into carbon nanotubes (CNTs) to protect the DNA from the ambient environment.

The GLIDP is generated between the bottom liquid and top metal electrodes in Ar gas (20 kPa) by applying a pulse voltage (20 kHz) to the liquid electrode. The liquid electrode consists of aqueous chloroauric acid trihydrate ($HAuCl_4 \bullet 3H_2O$) (0.1 mg/ml) with DNA. A single-stranded DNA is used as the conjugated material, which consists of 30 bases of cytosine or guanine. In the synthesis of the DNA-AuNP encapsulated CNTs, double-walled carbon nanotubes (DWNTs) are adopted to be used because of their large inner diameter.

Depending on the DNA concentration, the resultant water-soluble AuNPs take on pink and purple. The different colors originate from the particle size and interparticle distance which determine the absorption wavelength of the surface plasmon resonance of the AuNPs. Interestingly, these phenomena depend on the types of DNA base, which are attributed to the difference in the binding energy of the DNA base. Therefore, we can control the size and assembly of the AuNPs by changing the DNA type and concentration [3].

In order to encapsulate the negatively charged DNA-AuNPs into the DWNTs, a positive DC voltage is applied to the DWNTs put on the substrate immersed in the GLIDP. The transmission electron microscope images of the resultant products show that the number of the DNA-AuNPs encapsulated into DWNTs increases with an increase in the positive DC voltage.

[1] T. Kaneko, K. Baba and R. Hatakeyama: J. Appl. Phys. **105**, 103306 (2009).

[2] T. Kaneko, Q. Chen, T. Harada and R. Hatakeyama: Plasma Sources Sci. Technol. **20**, 034014 (2011).

[3] Q. Chen, T. Kaneko, and R. Hatakeyama: Chem. Phys. Lett. **521**, 113 (2012).

5:00pm **PS+BI-MoA10 Organization of Dielectric Barrier Discharges in the Presence of Structurally-Inhomogeneous Wood Substrates**, *O. Levasseur,* Université de Montréal, Canada, ***A. Bouarouri***, *N. Naudé, R. Clergereaux, N. Gherardi,* Université de Toulouse, UPS, INPT, LAPLACE, France, *L. Stafford*, Université de Montréal, Canada

There has been a growing interest in the use of dielectric barrier discharges (DBDs) for many applications, especially for the treatment of heat-sensitive materials such as polymers. Some studies have also reported a self-organization of these discharges which can manifest itself in two ways : i) the auto-organization of filaments or micro discharges in a filamentary DBD or ii) the formation of regular spatio-temporal patterns in a glow-like discharge. Several types of patterns such as hexagonal arrays or concentric rings have been observed for various gases and system configurations. We have recently extended the range of applications of DBDs to the functionalization of wood surfaces with the objective of improving its durability following natural weathering. However, the application of DBDs to the modification of wood presents additional complications compared to traditional substrates due not only to the highly porous nature of wood which can produce significant outgassing but also to the presence of "early" vs. "late wood" sections which can introduce local modification of the properties of the dielectric exposed to plasma. In this work, we examine the organization of DBD in the presence of complex wood substrates using optical imaging and current-voltage (I-V) characteristics. For Douglas pine samples, the structural inhomogeneities of the wood substrate was found to produce non-uniform light emission patterns while maintaining homogeneous-like I-V characteristics. Experiments performed on samples with various fractions of "early" vs. "late" wood sections showed that the plasma emission was always more intense on the "early" wood. The charge flow pattern was also analyzed using surface potential measurements. Both sections exhibited decaying behaviors, with time constants, t, of 40 s for late wood and 10 s for early wood. Based on these results and the predictions of a simple electrical model of the discharge, the organization was ascribed to a spatial modulation of the relative dielectric permittivity on "early" versus "late" wood affecting the local voltage applied to the gas, and thus the local discharge current which is directly related to the plasma emission.

5:20pm **PS+BI-MoA11 Role of Substrate Outgassing on the Formation Dynamics of Either Hydrophilic of Hydrophobic Wood Surfaces in Atmospheric-Pressure, Organosilicon Plasmas**, ***O. Levasseur***, *L. Stafford,* Université de Montreal, Canada, *N. Gherardi, N. Naudé,* Université de Toulouse, UPS, INPT, LAPLACE, France, *P. Blanchet,* FPInnovations, Canada, *B. Riedl,* Université Laval, Canada, *A. Sarkissan*, Plasmionique, Canada

Dielectric barrier discharges (DBDs) were thoroughly investigated over the last several years with one of the main goals being the achievement of a homogeneous discharge at high operating pressure in various gas mixtures. This keen interest is mainly driven by the fact that atmospheric-pressure DBDs present major advantages over low-pressure plasmas for polymer treatments, one of the most important being the ability to work with cold plasmas without the use of high-end vacuum pumping systems. Over the last decade many precursors, such as organosilicon compounds like hexamethyldisilazane (HMDSN) and hexamethyldisiloxane (HMDSO), were added to these cold, atmospheric-pressure plasmas for PECVD applications and a wide variety of coatings have been obtained by such methods. Application of DBDs to the treatment of polymers is however much more challenging than for conventional substrates such as Si or SiO2. This can be not only be attributed to the highly complex chemical nature of most polymers but also to their generally porous microstructure which can release impurities in the discharge either from plasma-substrate chemical reactions or from sample outgassing (if not pumped-down beforehand). Such impurities can greatly alter the discharge stability and gas-phase kinetics which are both known to play an important role on the plasma deposition dynamics. In this work, we capitalize on the very porous nature of wood to examine the influence of substrate outgassing during PECVD on the stability of a N_2-HMDSO discharge and on the evolution of the properties of plasma-deposited thin films over sugar maple and black spruce wood samples. Current-voltage characteristics revealed a transition from a filamentary to a homogeneous discharge with increasing plasma treatment time, *t*. Based on optical emission spectroscopy, the filamentary behavior was ascribed to the release of air and humidity from the wood substrate following plasma exposure which produced significant quenching of N_2 metastables. This effect vanished at longer treatments times due to the nearly complete "pumping" of products from the substrate and the progressive deposition of a "barrier" layer. Analysis of the surface wettability through static, water contact angles (WCAs) and of the surface composition through FTIR and XPS indicated that for $t < 10$ min, the wood surface was more hydrophilic due to the formation of a SiO_x layer, a typical behavior for HMDSO deposition in presence of oxygen. On the other hand, for $t > 10$ min, the static WCA increased from ~50º up to ~140º due to the deposition of hydrophobic $Si(CH_3)_3$-O-$Si(CH_3)_2$ and $Si(CH_3)_{3,2}$ functional groups.

Applied Surface Science
Room: 20 - Session AS+BI-TuM

Practical Surface Analysis
Moderator: A. Belu, Medtronic, Inc., D.L. Pugmire, Los Alamos National Laboratory

8:00am **AS+BI-TuM1 Clinical Application of Surface Analysis Technologies – Needs, Requirements and Challenges**, ***J. Schnekenburger***, Muenster University, Germany **INVITED**

Surface analysis technologies offer tremendous applications in clinical fields. The interface of cells and materials is a crucial determinant for implant integration, artificial organ regeneration and stem cell differentiation. Cells are highly sensitive not only to chemical but also to structural determinants of their environment. Material softness, roughness and distance of adhesion points are known factors for adhesion, differentiation and the maintenance of cell function. The characterization of cell environments and surfaces for advanced cell culture by surface analysis technologies is a key element of the successful generation of bioimplantable materials and tissue regeneration.

Dental implants and liver regeneration are high impact examples for surface analysis needs. Dental implants should have a structure and chemical composition which facilitates osteoblast adhesion and bone development but impairs microbial growth and adhesion. Different implants were characterized and cell adhesion presented. The regeneration of functional liver cells from mesenchymal stem cells would allow the replacement of donor organs by cell implants. Stem cell differentiation not only requires genetic reprogramming and soluble factors but also a three dimensional environment with key elements of mature hepatocyte surrounding. These surface structures need to be identified and transferred in tissue culture dishes.

The analysis of cells and tissues as materials is challenging. The clinical environment requires technology application processes different from material science. Clinical routine analysis is cost driven and performed by technicians or MDs without deeper technical training. Expert personnel are available only in high throughput clinical centers. Also research is based on understanding the molecular determinants like DNA and proteins rather than material aspects. Furthermore cells and tissues need preparation since biological material can not be measured in high vacuum. The preparation like chemical fixation limits the analysis to specific time points of biological processes and may alter the samples compared to the original state. The combination of technologies like mass spectrometry or scanning electron microscopy with atomic force microscopy or digital holography allows the analysis of preparation artifacts and the generation of reliable data.

Overcoming the current restrictions surface analysis technologies have the potential to replace the biomedical gold standard light microscopy and fluorescence microscopy in the high resolution and three dimensional structural and chemical analysis of biological samples.

8:40am **AS+BI-TuM3 The Application of XPS to the Study of Protein Lyophilizates**, ***S.J. Coultas***, *J.D.P. Counsell, A.J. Roberts, S.J. Hutton, C.J. Blomfield,* Kratos Analytical Ltd, UK, *R. Geidobler, G. Winter*, Ludwig-Maximilians-University, Germany

Long term storage of proteins is most often achieved by freeze drying (lyophilization). For this to be successful it is essential that the process retains the stability and biological activity of the protein. Despite its widespread use there are still problems associated with the process, not least the aggregation of the protein at the ice/liquid interface which develops during the freezing stage. To overcome this problem excipients are commonly used to ease the stresses at this interface and stabilise the protein. Polysorbates are commonly used for this purpose but there has been recent interest in using other excipients.

X-ray photoelectron spectroscopy (XPS) is ideally suited to the study of these materials due to its surface sensitivity (1-10 nm) and the quantitative nature of the data.

In this study we use XPS to investigate the protein stabilisation mechanism in lyophilizates produced using different excipients. We show there to be clear differences in the surface chemistry of the resultant lyophilizates. We also investigate the effect of temperature on the protein surface chemistry and stability.

9:00am **AS+BI-TuM4 Characterization of Real-World Surfaces and Interfaces of Devices in the Biomedical Industry**, ***W. Theilacker***, *A. Belu, L. Lohstreter, L. LaGoo*, Corporate Technology and Innovation, Medtronic, Inc.

This presentation will highlight the use of surface analysis methods for the characterization of medical devices. Examples will be presented to demonstrate a range of practical applications in solving industrial problems. A multi-technique approach is used to better understand issues of cleanliness, adhesion, and intentional surface modification with regards to pacemakers, leads, and other cardiovascular devices. Oftentimes the samples provided are non-ideal for surface sensitive techniques, e.g. they are large, non-flat, and have been handled, or have been in contact with other materials. This presentation will also address approaches for characterization of real-world, non-ideal samples. The surface is an important zone as it is the interface between a material of interest and its environment. Knowledge of interface chemistry is critical for understanding how a biomaterial or drug delivery system will interact with the biological environment of the body. For other materials, particularly those that are employed in the manufacture of medical devices, evaluation of the surface is important to further understand issues with welding, adhesion, contamination, discoloration, etc. Many techniques may be utilized in order to gain a comprehensive understanding of surface morphology and chemistry, including traditional techniques such as SEM-EDS (scanning electron microscopy energy dispersive spectroscopy), IR (infrared) spectroscopy, along with other techniques such as confocal Raman microscopy, interferometry, ellipsometry, XPS (x-ray photoelectron spectroscopy), and TOF-SIMS (time-of-flight secondary ion mass spectrometry). A comparison of the techniques will be made to help elucidate which method or methods are best for specific problems. Further, the power of and the problems with data acquisition and interpretation will be highlighted with regards to each technique.

9:20am **AS+BI-TuM5 Ageing Processes Occurring on Nanoscaled Aminated Surfaces as Observed by ToF-SIMS/PCA, NEXAFS Spectroscopy and XPS**, ***W.E.S. Unger***, BAM Federal Inst. for Materials Res. and Testing, Germany, *H. Min,* BAM Federal Inst. for Materials Res. and Testing and KAIST Korea, *S. Swaraj,* BAM Federal Inst. for Materials Res. and Testing and Soleil Synchrotron France, *P.-L. Girard-Lauriault,* BAM Federal Inst. for Materials Res. and Testing and McGill Univ. Toronto, *A. Lippitz*, BAM Federal Inst. for Materials Res. and Testing, Germany

Ultrathin organic surfaces covered by amines as coupling sites are often used in recent technologies as biosensing, adhesion in composite materials and layer-by-layer deposition of nano structures on self-assembled monolayer platforms. Ageing processes occurring with those aminated surfaces have to be regularly controlled in order to guarantee their functionality in applications.

We used a combined XPS, NEXAFS spectroscopy and ToF-SIMS/PCA approach to follow ageing of different kinds of amino-terminated surfaces stored on ambient air up to ~1 year. Test samples have been prepared as (1) aliphatic and aromatic aminosilanes on glass slides, (2) aminothiols prepared as self assembled monolayers and (3) by different plasma polymerization technologies (low pressure and atmospheric pressure DBD plasma polymerization).

The observation common to all investigated films is that the ageing process ends with a formation of amides which has been clearly proven by NEXAFS N K-edge spectra and PCA of ToF-SIMS data. However the kinetics of the ageing processes, the decay of amines, has been found to be rather different for the different kinds of samples investigated. The susceptibility of plasma deposited films is much higher the due to the radicals inherently produced by the deposition technique. Furthermore storage conditions have been found at which the decay of amines in course of ageing can be suppressed to some extent.

9:40am **AS+BI-TuM6 Signature Discovery in Explosives and Bioagents using Imaging Mass Spectrometry**, ***C.M. Mahoney***, Pacific Northwest National Laboratory

Recent terrorist attacks, both in the US and abroad, have indicated that significant improvements in intelligence operations are required for adequate prevention and prosecution of terrorist acts. This includes the ability to accurately and rapidly attribute pre-detonated and post-detonated explosive devices and/or other weapons-based material to a particular source, and/or region of the world. Surface mass spectrometry methods have the potential to greatly advance the field of forensics science, allowing for simultaneous elemental, isotopic and molecular imaging on a sub-micron to nano-scale range, with superior chemical specificity and

sensitivity. With recent advancements in the field of surface mass spectrometry, the versatility of these methods has increased dramatically, allowing for the direct analysis of samples at atmospheric pressure (e.g. Desorption ElectroSpray Ionization or DESI). The potential for 3-D molecular analysis in soft samples with depth resolutions on the order of 5 nm has also been realized with advent of the gas cluster ion beam (GCIB) source. Finally substantial improvements in the mass resolving power (by at least a factor of 10) has been observed when employing FT-MS mass spectrometers, allowing for even greater improvements in the chemical specificity. Here we describe our efforts to develop a suite of advanced mass spectral analysis and imaging techniques for the characterization and attribution of plastic explosives and other complex explosive mixtures from around the world. We will also provide initial feasibility studies for the characterization and differentiation of biological agents based on their unique molecular fingerprints. With the development of these very powerful "chemical signature microscopes" it is expected that significant advancements will be made in the field of forensics, both on the home front, and abroad.

10:40am **AS+BI-TuM9 Topography and Field Effects in the Inner Side of Micro via Hole using ToF-SIMS**, ***J.C. Lee***, *Y.K. Kyoung, I.Y. Song,* Samsung Advanced Institute of Technology, Republic of Korea*, S. Iida*, Ulvac Phi, Japan

Surface topography is often important role in the functionality and activity of electronic devices including MEMS, composite materials, catalysts, sensors, biomedical, and packaging of semiconductor devices. Especially, trench structure such as via hole or etched pattern is one of the important processes in the through silicon via or ball grid array. If there is contaminated on the wall or bottom of via hole, it may cause contact failure between integrated circuits and printed circuit board (PCB) because of increasing contact resistance. For the recent decade, many research activities are focused on the quantitative analyses of topographic samples using TOF-SIMS. However, the most of results were focused on the nanowire, nano particle, and etched surface, it is relatively rarely dealt with the trench shape sample. It is not easy to characterize the contaminant level of ~ppm or less on the bottom of trench shape sample such as via hole. It is well known that a ToF-SIMS is one of powerful tools to analyze organic contaminants. However there are some limitations to apply it to the trench shape sample because of high sample bias voltage and short focal length of emersion lens of ToF-SIMS analyzer. If we want to characterize contaminants on the bottom of via hole using a ToF-SIMS, the side wall of via hole should be removed by mechanical treatments. In this study, we aim to establish an optimized method that is able to characterize the bottom and wall of via hole of BGA using ToF-SIMS without any mechanical or chemical treatments. This is performed by combining ToF-SIMS experiments using via hole systems with computer modeling using SIMION.

For this study, trench structure samples with the diameter of 90μm and width of 90μm were used for TOF-SIMS imaging. Via holes were fabricated by laser drilling method. Samples were mounted on the sample holders which were specially designed with tilted angles of 15, 28, and 40 degrees surfaces for this experiment. Secondary ion trajectory and potential contour were calculated using SIMION for 0, 15, 28, 40 degree tilted samples for understanding the angle dependence of field effects.

According to the simulation results, secondary ions ejected from near corner between wall and bottom of via hole are aimed to diagonal direction due to Coulomb repulsive force between secondary ions and wall of via hole. When specially designed 40 degree tilted angle sample holder which is based on simulation result is used, the bottom and wall of via hole of BGA can be fully characterized using ToF-SIMS without any mechanical treatment.

11:00am **AS+BI-TuM10 Using XPS to Probe the Surface Chemistry of Ionic Liquids**, ***J.D.P. Counsell***, *S.J. Coultas, A.J. Roberts, S.J. Hutton, C.J. Blomfield*, Kratos Analytical Ltd., UK

Ionic liquids have attracted much attention due to their possible "green chemistry" applications. Due to the recent use of ionic liquids as corrosion resistant thin-films, it has become important to fully understand the complex nature of their surface environments.

A series of commercially available ionic liquids (e.g. [BMIM][PF_6]) were studied and characterised using x-ray photoelectron spectroscopy. Angle-resolved experiments indicate an increased concentration of the organic cation in the liquid's surface. The surface composition becomes enriched with contributions from the linear alkyl substituent of the cation which is significantly greater than that expected from the nominal stoichiometry. A maximum entropy method algorithm was used to build an accurate structure of the surface and near-surface region

We also explore the possibilities of using ionic liquids as potential new reference standards. They present the opportunity to offer a clean reference surface without the need for ion sputtering and present a number of core level peaks for spectrometer energy scale and transmission function calibration and validation.

11:20am **AS+BI-TuM11 XPS Profiling and Work Function Mapping of a Damaged Solar Cell**, ***B. Strohmeier***, Thermo Fisher Scientific*, P. Mack, T.S. Nunney, J. Wolstenholme*, Thermo Fisher Scientific, UK

In many areas of materials technology, it is important to control both the chemical composition and the electrical properties of the material. One example of this need is in the manufacturing of solar cells. In this case, the solar cell is based on a thin film of CIGS (Cu (In, Ga) Se2). The full structure of the device includes an upper electrode containing indium tin oxide (ITO), zinc oxide, and cadmium sulfide. The whole structure is separated from a steel substrate using layers of molybdenum and chromium.

It has been demonstrated previously that X-ray Photoelectron Spectroscopy (XPS) is the ideal technique for characterizing the compositional depth profiles of CIGS solar cells, similar to the one described above. Using XPS it is possible to measure elemental composition gradients in the CIGS layers (allowing engineers to tune the band gap of the device) and also to investigate chemistry at interfacial layers. XPS can also be used to measure another very important parameter of solar cells, i.e. the work function. This measurement relies upon the spectrometer being accurately calibrated and the photon energy being accurately known. On a modern XPS instrument, internal standard samples (copper, silver, and gold) may be used to automatically calibrate the XPS binding energy scale. The photon energy can be checked by measuring the position of an X-ray induced Auger peak on the binding energy scale and adding it to the known kinetic energy for that peak in the Auger spectrum.

This work demonstrates the use of XPS to characterize a damaged solar cell, using depth profiling to identify the delamination zone in the solar cell stack. The surface of the delaminated cell has also been mapped for elemental and work function information.

11:40am **AS+BI-TuM12 Application of XPS Imaging Analysis in Understanding of Interfacial Delamination and Related Problems**, ***H. Piao***, General Electric Global Research Center*, N. Fairley,* Casa Software Ltd, UK*, J. Walton*, The University of Manchester, UK

The recent development of X-ray Photoelectron Spectroscopy (XPS) instrumentation with near-micron spatial resolution has advanced the capability of elemental and chemical state imaging. This work extends the application of imaging XPS to the analysis of real world samples. The presentation also focuses on description of radiation damage of polymers encountered in XPS imaging analysis. The imaging analysis can cause extensive damage to polymers since the acquisition time for creating datasets can be excessive. Understanding of radiation damage in polymers is necessary for successful and validated application of XPS spectromicroscopy.

Keywords: XPS, chemical states, imaging, delamination.

Biomaterial Interfaces
Room: 23 - Session BI+SS+AS-TuM

Biomolecules at Interfaces
Moderator: P. Kingshott, Swinburne University of Technology, Australia

8:20am **BI+SS+AS-TuM2 Computer Simulation of Water-Mediated Adhesion between Organic Surfaces**, *A.J. Pertsin,* ***M.H. Grunze***, University of Heidelberg, Germany

The adhesive forces operating between various surfaces in aqueous media are of interest in many areas ranging from biology to electronics. This refers, in particular, to surfaces formed by self-assembled monolayers (SAMs) on solid substrates to modify the surface-sensitive properties of the latter. Another important example is provided by supported lipid bilayers, where the water-mediated bilayer-substrate adhesion determines the stability of the system. The present study is concerned with surfaces formed by a hydrophobic methyl-terminated SAM (C-SAM), a hydrophilic carboxyl-terminated SAM (hereafter, O-SAM), and a phosphatidylethanolamine (PE) bilayer. The surface-water-surface system was treated as an open one using the grand canonical Monte Carlo technique. The free energies of adhesion were evaluated by integration of simulated pressure-distance relations. For SAMs, both symmetric and asymmetric confinements were considered, as formed by like and unlike SAMs, respectively. As the confinement was increased, water confined by the C-SAMs experienced capillary evaporation. As a consequence, the adhesion energy was mainly determined by the direct interaction between

bare C-SAMs. In the asymmetric SAM system, an incomplete capillary evaporation was observed, with the number of water molecules dropped by more than an order of magnitude. The remaining water molecules were all adsorbed on the O-SAM, while the C-SAM was separated from the rest of the system by a thin vapor layer. The calculated free energies of adhesion were in acceptable agreement with available experimental data. Unlike the SAM systems involving the hydrophobic C-SAM, the PE/water/C-SAM system did not experience capillary evaporation up to the highest confinements tried. A likely reason is a high molecular-level "roughness" of the PE/water interface due to a deep penetration of water in the PE bilayer. The pressure-distance dependence showed a slightly repulsive region with a depth comparable with the statistical uncertainty in pressure. By contrast, the pressure-distance curve of the PE/water/O-SAM system showed a well-defined minimum with a depth of about 0.7 kbar. The integration of this curve resulted in an adhesion free energy of 19±3 mJ/m^2, close to the value obtained for the O-SAM/water/O-SAM and O-SAM/water/C-SAM systems (~25 mJ/m^2).

8:40am **BI+SS+AS-TuM3 Adsorption from Saliva - Properties of Adsorbed Layers and Comparison with Other Systems**, ***T. Arnebrant***, *L. Lindh, J. Sotres*, Malmö University, Sweden **INVITED**

Adsorbed salivary protein layers will cover soft and hard surfaces in the oral cavity, where they fulfill a protective function influencing adhesion and wear, and also surfaces of devices exposed to saliva. Properties of salivary films will depend on the characteristics of the surface on which they are formed as well as solution conditions (salt, pH) and will affect surface properties such as wettability and charge. Moreover, normal and lateral forces between surfaces bearing salivary films will be distinctly different than for bare surfaces. Such changes in surface properties and interactions may be relevant not only for events at oral interfaces but also for the operation of monitoring or sampling devices immersed in or exposed to saliva. Here, we show how a combined characterisation of these systems through different surface techniques provides important information on the role of this body fluid which is not available through more common chemical or biochemical approaches. The presentation will describe adsorption characteristics of salivary proteins from the total secretion as well as for purified fractions including single protein preparations. Influence by surface properties and ambient (solution) conditions will be outlined. Data on structure of salivary films as obtained by *in situ* ellipsometry, QCM-D and neutron reflectivity will be reported. Furthermore, SFA and AFM measurements of DLVO, steric, adhesive and frictional forces between surfaces bearing salivary films will be discussed. A new method for estimating the strength of salivary films based on simultaneous recording of roughness and friction data from AFM will also be described.

References: Protein Adsorption in the Oral Environment, Arnebrant T, In Biopolymers at Interfaces 2nd ed. (M. Malmsten Ed.) Marcel Dekker, 2003, pp 811-856

Friction force spectroscopy as a Tool to Study the Strength and Structure of Salivary Films. Sotres J., Liselott L., Arnebrant T. 2011. *Langmuir, 27 (2011), 13692-13700.*

9:20am **BI+SS+AS-TuM5 An Atomic Force Microscopy Based Method for the Determination of Protein Stability**, *O. Croad,* Univeristy of Nottingham, UK, *S. Rigby-Singleton,* Molecular Profiles Ltd., UK, *C.J. Roberts, D.J. Scott, P.M. Williams,* ***S. Allen***, University of Nottingham, UK

A method for the early detection of instability and aggregation propensity of proteins and other biological macromolecules would be valuable for the rapid development of novel biopharmaceutical formulations. The aim of this study was to investigate the potential of atomic force microscopy (AFM) based adhesion force measurements to meet this need. We report the first key step in demonstrating this approach; a clear relationship between how frequently an AFM probe adheres to a protein coated surface and the fraction of unfolded proteins on that surface. Instability and subsequently protein denaturation are commonly linked with protein aggregation, and hence formulation failure. It was found that for the protein bovine serum albumin (BSA), the adhesion between AFM tips and protein-coated samples occurred much more frequently as either the concentration of a denaturant or temperature was gradually increased. We compared this behaviour with fluorescence based studies of the BSA unfolding in solution. Both methods provided us with almost identical ΔG values of stability and 50% unfolding ($[D]^{50\%}$) values. The data demonstrates for the first time, an AFM based method for protein stability determination. Interestingly, the method also appears to be a good reporter of the protein solution behaviour. With further development this approach could be utilized to screen for instability and aggregation propensity of a given protein therapeutic, in a range of conditions. The ultimate aim is to create a robust technique that can be performed rapidly and routinely.

9:40am **BI+SS+AS-TuM6 Von Willebrand Factor A1 Domain Structure and Function Changes on Surfaces**, *E. Tronic, W. Thomas,* ***D.G. Castner***, University of Washington

The clotting protein von Willebrand Factor (VWF) binds to platelet receptor glycoprotein 1ba (GP1ba) when VWF is activated, such as when VWF is exposed to a surface or is under high shear. However, the mechanism of surface activation is not known. This study characterizes function and adsorption behavior of the VWF A1 domain, which contains the GP1ba binding site. Surfaces tested are glass, polystyrene, and tissue culture polystyrene. Highest VWF A1- GP1ba binding is observed when A1 is adsorbed onto polystyrene, as measured by platelet rolling velocity in a parallel plate flow chamber assay. X-ray photoelectron spectroscopy (XPS) showed comparable A1 amounts are present on each surface, suggesting functional differences were not explained by differences in surface coverage. A1 surface structure was investigated using ELISA, time-of-flight secondary ion mass spectrometry (ToF-SIMS) and near-edge x-ray absorption fine structure (NEXAFS). Using monoclonal antibodies binding to a nonlinear epitope within A1, ELISA showed lower antibody binding for A1 adsorbed to polystyrene than to glass or tissue culture polystyrene. ToF-SIMS was used to identify differences in amino acid exposure, and NEXAFS showed different amide backbone ordering on the three surfaces. These studies demonstrate that the surface dependence of A1 function is likely due to differences in adsorbed surface orientation and/or conformation. This is an important consideration in *in vitro* models, where A1 is typically immobilized onto synthetic surfaces, and is also of interest for blood-contacting biomaterials. Additional studies have been done on A1 and two A1 mutants adsorbed on collagen coated tissue culture polystyrene. One mutant exhibits similar ELISA and ToF-SIMS results to the wild type A1, while the other mutant exhibits differences. This indicates that mutations in A1 can affect the conformation/orientation changes that result from A1 adsorption onto collagen.

10:40am **BI+SS+AS-TuM9 Combining Catalysis and Self-Assembly: Towards Evolvable Soft Matter**, ***R. Ulijn***, University of Strathclyde, UK **INVITED**

Molecular networks are key to the adaptiveness of biological systems and it would be very useful if this concept could be introduced into simple man-made functional materials, which could adapt to changing environments. In biology, adaptiveness (as a consequence of evolution) is achieved through a combination of catalysis, self-assembly, molecular recognition and compartmentalisation. These individual molecular processes are closely linked, a situation which may be achieved in laboratory based systems by sharing of building blocks between these individual processes, thereby giving rise to networked systems that are highly responsive and adaptive to changing external conditions. We have made the first steps towards developing evolvable materials, and will present progress in (i) structure/function relationships in peptide self-assembly, (ii) development of catalytic peptides, (iii) self-selecting peptide libraries achieved by combining fully reversible amino acid exchange in self-assembing peptide systems. The overall aim of this area is to produce laboratory made molecular materials that incorporate the above features and are able to adapt and change their properties in response to external environmental changes. Potential applications in biomaterials science will be discussed.

11:20am **BI+SS+AS-TuM11 Bio/Nano Interfaces of De Novo Design: Small Proteins with Large Potential**, ***M.G. Ryadnov***, National Physical Laboratory, UK

Our ability to manipulate function at interfaces in native and near-native environments is critical for the fabrication of nanostructured materials and devices. Biomolecular self-assembly lends itself to robust bio-nano systems. However, exact construction strategies to enable desired applications stumble upon the lack of control over self-assembly processes. De novo peptide design provides a saving solution to this.[1] Small proteins can be designed to deliver functions that are otherwise accessible only to macromolecular subcellular complexes. Examples include gene delivery systems,[2] fibrillar microscopic structures for tissue repair[3] and responsive antimicrobial agents[4]. A key factor in all such designs is their structural and functional relevance to native self-assembling structures, be these viruses, extracellular matrices or host defence systems. Thus, this is our ability to construct such materials at will that advances the development of efficient bio/nano-interface technologies.[5] **References** 1. Ryadnov, M. G. (2012) Prescriptive peptide design. In ***Amino acids, peptide and proteins***. (Farkas, E. & Ryadnov, M. G., eds.) SPR, RSC Publishing (2012), v.37. 2. Lamarre, B., Ravi, J. & Ryadnov, M. G. (2011) GeT peptides: a single-domain approach to gene delivery. ***Chem. Commun.***, 47, 9045-9047. 3. Bella, A., Ray, S., Shaw, M. & Ryadnov, M. G. (2012) Arbitrary self-assembly of peptide extracellular microscopic matrices. ***Angew. Chem. Int. Ed.***, 51, 428-431. 4. Ryadnov, M. G., Mukamolova, G. V., Hawrani, A. S., Spencer, J. & Platt, R. (2009) RE-coil: an antimicrobial peptide regulator.

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11:40am **BI+SS+AS-TuM12 Application of CD and SRCD Techniques to the Study of Protein/Nanoparticle Complexes**, ***G. Ceccone****, S. Laera, L. Calzolai, D. Gilliland,* EC-JRC-IHCP, Italy*, R. Hussein, G. Siligardi,* Diamond Light Source, UK*, F. Rossi*, EC-JRC-IHCP, Italy

Nanotechnology is having a large impact in very different scientific fields and the use of nanotechnology-based materials is not just limited to research laboratories, but has already been applied in several industrial sectors and into real products as disparate as medical diagnostic tools, drug delivery systems, cosmetics, and consumer products.

In particular, engineered nanoparticles (ENPs) are used in different applications such as cosmetics, food and medicine and currently more than 600 products containing nanomaterials are already on the market[1,2,3]. At the same time there is a growing public concern about the safety of ENPs since it has been demonstrated that those intended for industrial and medical applications could cause adverse effects in mammalians or aquatic organisms by specific mechanisms depending on their physical chemical properties[4]. However, the interaction of nanomaterials with complex matrices is far to be understood. In fact, although it is now increasingly accepted that the surface of nanoparticles in a biological environment is modified by the so called "protein corona"[5,6], the importance of the detailed structure of the adsorbed protein-solution interfaces is still not much addressed in the nanotoxicology literature[7] .

In this work, we report the use of Circular Dichroism (CD) and Synchrotron Radiation Circular Dichroism (SRCD) to detect changes in the secondary structure and stability of different classes of proteins interacting with nanoparticles. In particular, we show that by using the SRCD we can detect structural changes of proteins in the nanomolar concentration range when they form protein-nanoparticle complexes[8]. Furthermore, the adsorption of protein on NP modifies their melting point in a composition and size dependent manner, indicating once more that the protein corona formation is strongly depending on the nanoparticles physico-chemical properties. For instance, while the presence of Au NPs do not influence the thermal unfolding process of human serum albumin (HSA), a significant decrease of the HSA melting temperature (about 6ºC) is observed in presence of Ag NPs.

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Tribology Focus Topic
Room: 19 - Session TR+BI-TuM

Self Healing Coatings, Bio-Inspired Design, and Frictional Properties of Biological Materials

Moderator: D. Irving, North Carolina State University, M.O. Robbins, Johns Hopkins University

8:20am **TR+BI-TuM2 Friction at Hydrogel Contact Lens Surfaces**, ***S.S. Perry****, S. Huo, A. Rudy*, University of Florida **INVITED**

The surfaces of six types of silicone hydrogel (SH) contact lenses (PureVision®, O_2 OPTIX®, ACUVUE® Oasys ®, ACUVUE® TruEye®, Biofinity®, DAILIES TOTAL1®) and the pHEMA-based ACUVUE® 2 have been analyzed using atomic force microscopy (AFM) in aqueous environment. The elastic modulus, frictional, and adhesive properties of each lens were evaluated using calibrated instrumentations, providing a basis for comparing the distinctive surface properties of these lenses. Cantilevers modified with 5-µm (diameter) silica colloidal probes were employed throughout the experiments. Elastic modulus was measured by indenting the probe into the surface of the hydrogel in a controlled manner (i.e. approach speed and maximum applied force), such that the maximum indentation depth was restricted to sub-micron levels. A modulus value was obtained by fitting the characteristic force versus indentation behavior to a mathematical model. The frictional force was measured for the sliding contact of the probe and the surface at the length scale of 500 nm and with applied loads up 20 nN. The friction coefficient was realized by evaluating the linear dependence of friction force on applied normal load. The lenses examined exhibited an order of magnitude difference—from the softest to the stiffest sample—in modulus value, generally reflective of the distinct surface treatments they received during manufacturing. For example, the pHEMA-based ACUVUE® 2 was shown to have a modulus between 100 and 130 kPa, whereas PureVision®'s was an order of magnitude higher in value. The frictional properties of the lenses followed a similar trend in that the lenses with surface treatment, such as PureVision® and O_2OPTIX®, generally exhibited coefficients of friction five times greater than that of a non-treated lens such as ACUVUE® OASYS®. The elastic modulus and frictional properties of different lenses evaluated on a nanoscopic level by AFM depict a strong correlation between the surface treatments and the apparent mechanical behaviors of the lenses.

9:00am **TR+BI-TuM4 Linking Cartilage Structure, Lubrication, and Osteoarthritis**, ***D.L. Burris***, University of Delaware

Cartilage is known for exceptionally low friction coefficients during sliding, but its wear resistance is arguably more remarkable. Conventional wisdom suggests that cartilage wears gradually with use and that osteoarthritis is the inevitable consequence. This notion is refuted by the scientific literature. Dissections of mature, healthy, and active joints consistently reveal smooth, glossy, damage-free articulating surfaces that can only occur if tissue recovery matches wear. Cartilage recovery is extremely slow due to a lack of vasculature and numerous lubrication mechanisms have been proposed to explain extremely low in-vivo wear rates. Osteoarthritis (OA) is characterized by progressive wear and caused by a system destabilizing input (*e.g.* biochemistry, acute injury, altered loading, and joint instability). In certain joint-destabilized animal models, for example, a localized defect (~50 µm wide) is visible in as little as a week, and bone-on-bone contact occurs on the order of 6 months. Recent studies suggest that interstitial lubrication, a mechanism that reduces frictional and normal stresses by nearly 100X, is the dominant protective mechanism of cartilage. Localized surface damage can disrupt the very specific structural features responsible for the unique interstitial fluid pressurization mechanism. We hypothesize that localized surface damage can initiate OA-like degradation if it is sufficiently disruptive to the interstitial lubrication mechanism. In this paper, we present friction and wear measurements designed to explore this novel mechanical hypothesis of OA initiation and progression.

9:20am **TR+BI-TuM5 Self Healing Materials: A New Approach to Make Materials Perform More Reliably under Harsh Conditions**, ***S. van der Zwaag****, M. Valefi, S. Garcia, M.R. de Rooij*, Delft University of Technology and University of Twente, the Netherlands **INVITED**

Currently all engineering materials are designed on the basis of the 'amage prevention' paradigm i.e. the microstructure is designed such that damage forms as late as possible and grows slowly, but no mechanisms are built in which can reduced damage once formed. Materials in nature on the other hand seem optimised on the basis of 'damage management' paradigm, i.e. the occurrence of damage is taken as unavodidable and the material has the in-built ability to repair the damage during less demanding stages of the loading cycle. In this presentation we will show various approaches to self healing behaviour in a wide range of material classes and also show how self healing concepts can be used to mitigate tribological damage in both ceramics and polymeric materials. The experimental results are supported by a simple mechanical model.

10:40am **TR+BI-TuM9 Surface Analytical and Tribological Characterization of Diamonlike Boundary Films Extracted from Base Mineral and Synthetic Oils**, ***A. Erdemir****, O.L. Eryilmaz*, Argonne National Laboratory

In this study, we explored the possibility of deriving carbon-based bounary films directly from base lubricating oils during tribological tests. For this purpose, we first designed and deposited a series of catalytically active nanocomposite coatings on some steel substrates and by adjusting the ratios of softer phases made out of known catalysts and harder nitride phases (that are also catalytically active), we were able to extract carbon-based boundary films from the base oil molecules and deposit them as protective boundary films on rubbing surfaces. Using UV Raman and variety of other surface and structure analytical techniques,we were able to confirm that these boundary films were indeed similar to those diamonlike carbon films that are typically synthesized using CVD and PVD methods. Some of the main characteristics of resultant DLC boundary films were: very low friction coefficients (less than 0.05) even under extreme sliding conditions and very high resistance to wear and scuffing. In this paper, we will provide insight into the structural and chemical nature of these tribofilms and explain fundamental mechanisms for their impressive tribological properties under severe test conditions.

11:00am **TR+BI-TuM10 Data-driven Model for Estimation of Friction Coefficient via Informatics Methods**, *E.W. Bucholz,* University of Florida, *C.S. Kong,* Iowa State University, *K.R. Marchman, F.-Y. Lin, W.G. Sawyer, S.R. Phillpot,* University of Florida, *K. Rajan,* Iowa State University, ***S.B. Sinnott***, University of Florida

The rapid development of new mechanical assemblies capable of operating in extreme conditions requires the rapid determination/estimation of friction. Often, during the design phase, materials friction coefficients are unknown. Here, data mining and materials informatics methods are used to generate a predictive model that enables efficient high-throughput screening of ceramic materials, some of which are candidate high-temperature solid-state lubricants. Through the combination of principal component analysis and recursive partitioning using a small dataset comprised of intrinsic material properties, we develop a decision tree based model comprised of if-then rules, which estimates the friction coefficients of a wide range of materials derived from the interrelationships between the intrinsic material properties. This predictive model lays the foundation for new studies in predictive modeling and tailoring materials with specific tribological characteristics. It is applied to predict the tribological performance of a range of different materials.

This work is supported by the Office of Naval Research.

11:20am **TR+BI-TuM11 Structure, Lateral Flow, and Self-Healing of a Bound-and-Mobile Lubricant Film**, ***S.H. Kim***, Pennsylvania State University **INVITED**

There have been a significant amount of efforts to develop boundary lubrication films that have the bound and mobile natures at the same time. As an effort to develop a more efficient boundary film lubrication method, a new bound-and-mobile lubricant molecule was synthesized and its lubrication and self-healing capability was studied. Low-molecular-weight silicone molecules with cationic side groups can form bound-and-mobile boundary lubrication film on silicon oxide surface. Both nano- and macro-scale tribological tests revealed superior lubrication performance of the silicone polymer with cationic side chains (called cationic lubricant polymer, CPL) over the neutral silicone oil. The multilayer CPL films exhibited characteristic topographic features due to ionic interactions within the polymeric film. In the macro-scale, the effects of ionic content and environmental condition on self-healing will be discussed to demonstrate the wear resistance and self-healing capability. In the nanoscale, the results of disjoining pressure and viscosity measurements help understand the lateral spreading of the mobile layer and identify the mobile species. The CPL-coated surfaces are hydrophobic which prevents the detrimental effects of humidity on wear of silicon. In addition, the hygroscopic nature of CPL allows humidity to be absorbed into the film, which enhances the self-healing capabilities. By texturing the silicon surface with nanowells, self-healing can be enhanced when the nanowells are filled with CPL. The nanowells serve as CPL reservoirs that are readily available for self-healing within the wear track for faster cycle intervals. However, the nanowells deteriorate the self-healing from surrounding the contact region due to the refilling of the empty nanowells.

Applied Surface Science
Room: 20 - Session AS+BI-TuA

Surface Analysis of Materials Using Vibrational Techniques (2:00-3:20 pm)/ Multi-Technique Analysis (4:00-6:00 pm)

Moderator: D. Roy, National Physical Laboratory, UK, C. Szakal, National Institute of Standards and Technology

2:00pm **AS+BI-TuA1 Vibrational Spectrum and Stability of the Long-Debated Models for the (√7×√7)R19° Phase of S/Cu(111)**, ***M. Alcantara Ortigoza***, *M. Aminpour, T.S. Rahman*, University of Central Florida

Recently, the structure of the copper sulfide overlayer formed on Cu(111) upon sulfur exposure has attracted attention because it serves as a substrate to form MoS_2 monolayers and MoS_x nanostructures in a controlled manner, which may have numerous technological applications. In the past, at least eight experimental techniques have been used to characterize the (√7×√7)R19° Cu-S overlayer on Cu(111) and to support or refute a large number of possible models but, as yet, at least three models are still in dispute. In this study, we provide firmer arguments to resolve the structure of CuS/Cu(111) at the atomic scale. Specifically, we perform density-functional-theory calculations of the total energy and the vibrational spectrum of the proposed structures to (1) attest their dynamical stability; (2) compare their thermodynamic stability as obtained from the total free energy; and (3) provide the vibrational frequencies that uniquely fingerprint these structures and which may serve for further experimental confirmation or refutation.

This work was supported in part by DOE grant DE-FG02-07ER15842

[1] Kim et al., Langmuir 27, 11650 (2011)

[2] Alfonso J. Phys. Chem. C 115, 17077 (2011)

2:40pm **AS+BI-TuA3 First-principle Investigation of the Stability and Vibrational Spectrum of MoS_x Nanostructures Grown on Cu(111)**, ***M. Aminpour***, *M. Alcántara Ortigoza, T.S. Rahman*, University of Central Florida

Recent experiments have successfully synthetized MoS_X nanostructures in a controlled manner by evaporating Mo adatoms on the copper sulfide monolayer that forms on Cu(111) upon sulfur preloading[1,2]. Based on STM observations and total-energy calculations based on density functional theory, including ab intio van-der-Waals interactions, several structures for MoS_X/Cu(111) have been proposed. In this study, we investigate the plausibility of those structures and provide elements for further experimental substantiation or refutation. Namely, we perform density-functional-theory calculations (also including *ab intio* van-der-Waals interactions) of the total energy and the vibrational spectrum of the proposed structure to (1) attest their dynamical stability; (2) compare their thermodynamic stability as obtained from the total free energy; and (3) provide the vibrational frequencies that uniquely fingerprint the proposed structures.

[1] Kim et al., Langmuir 27, 11650 (2011)

[2] Le et al., PRB 85, 075429 (2012)

This work was supported in part by DOE grant DE-FG02-07ER15842

4:40pm **AS+BI-TuA9 New Desorption Mass Spectrometry Approaches for Inorganic Particle Analysis**, ***C. Szakal***, *A.R. Konicek, M. Ugelow, D.S. Simons, A. Herzing, R.D. Holbrook*, National Institute of Standards and Technology

Chemical characterization of inorganic particles becomes more difficult as the particle sizes decrease. For application areas ranging from semiconductor failure analysis to nanotoxicology, the distinct chemical signatures of both the surface and bulk of particles can provide insight into system mechanisms and behavior. New methods that aim to explore the surface chemistry of inorganic nanoparticles for both their elemental and organic overlayer signatures will be presented. Specifically, the "static" nature of time-of-flight-secondary ion mass spectrometry is used to provide mass spectral characterization at the very surfaces and sub-surfaces of well-prepared (via drop-on-demand inkjet printing) and well-characterized (via scanning transmission electron microscopy and ultraviolet-visible spectroscopy) nanoparticle aggregates. This information can potentially be combined with full aggregate analysis using more elementally sensitive dynamic SIMS instrumentation once target species are identified with ToF-SIMS. Both sets of SIMS data can be used to obtain a chemical distribution of signals throughout the particle depths. Additionally, the question of whether the centers of inorganic nanoparticle aggregates are chemically similar to the overall aggregate surfaces will be explored.

5:00pm **AS+BI-TuA10 TOF SIMS Analyses of Ga Concentration as a Function of Distance from FIB Milled Features**, *C. Santeufemio,* University of Massachusetts, *B.P. Gorman,* Colorado School of Mines, *C. Zhou, F.A. Stevie,* North Carolina State University, ***L.A. Giannuzzi***, L.A. Giannuzzi & Associates LLC

Focused ion beams are routinely used for site-specific specimen preparation, nanopatterning, and analysis. It is important to know whether the primary ion beam is present outside the region targeted for ion beam modification. A previous report showed that > 1E12 atoms/cm^2 of Ga was detected up to several millimeters away from a focused ion beam (FIB) milled feature [1]. In this work, we reproduce this earlier report using a blind study of 2 different state-of-the-art Ga-FIB columns. Each column was used to FIB mill a 100 µm x 100 µm square into a (100) Si wafer at 30 keV with a nominal beam current of 20 nA at constant dose. Time of flight secondary ion mass spectrometry (TOF SIMS) was used to measure Ga depth profiles and Ga surface concentration at a distance up to 6.5 mm from the FIB milled square. In column "A," > 1E12 atoms/cm^2 of Ga was detected up to ~ 5 mm from the FIB milled square. Column "B" showed considerably less Ga with > 1E12 atoms/cm^2 detected within ~ 250 µm from the FIB milled square. The depth profiles show that the Ga concentration was fairly uniform to a depth of ~ 2 nm from the surface for column "A" and ~ 1 nm into the surface for column "B". Using SRIM [2] simulations we determine that these implantation depths correspond to an ion energy < 500 eV. The consequences of the presence of Ga at long distances from desired FIB milled features will be discussed.

[1] U. Muehle, R. Gaertner, J. Steinhoff, W. Zahn, "Characterisation of Ga-distribution on a silicon wafer

after inline FIB-preparation using inline ToFSIMS," M. Luysberg, K. Tillmann, T. Weirich (Eds.): EMC 2008, Vol. 1: Instrumentation and Methods, pp. 749–750, DOI: 10.1007/978-3-540-85156-1_375, © Springer-Verlag Berlin Heidelberg 2008

[2] www.srim.org

5:20pm **AS+BI-TuA11 The Surface Characterization of Oligo(Ethylene Glycol) Functionalized Gold Nanoparticles**, ***A. Rafati***, *D.G. Castner*, University of Washington

Extensive surface analysis of available gold nanoparticles (AuNPs) is crucial to understand how their production and functionalization affects their final properties. This information is needed to improve the performance of engineered nanoparticles in research and commercial applications. Ethylene glycol functionality is desirable owing to the benefits such as the reduction of protein adhesion which if not properly controlled can lead to activation of an immune response and/or clearance.

In this work AuNPs ~14nm and ~40nm in diameter are synthesized and functionalized with 1-undacanethiol $(HS\text{-}CH2)_{11}$ terminated with either $(OEG)_4OH$ or $(OEG)_4CH_3$. The AuNPs were characterized with transmission electron microscopy (TEM), time of flight secondary ion mass spectrometry (ToF-SIMS), X-ray photoelectron spectroscopy (XPS), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) and low energy ion scattering (LEIS). These studies provided both qualitative and quantitative information about the functionalization of the AuNPs with an OEG containing monolayer.

TEM showed the 14nm AuNPs had a narrower size distribution and more spherical shape than the 40nm AuNPs. ToF-SIMS clearly differentiates the two SAMs based on the $C_3H_7O^+$ peak attributed to the CH_3 terminated SAM. Angle-resolved XPS high-resolution C1s spectra from flat gold samples at photoelectron take-off angles of 0˚, 55˚ and 75˚ from the surface normal shows an increase in the ether component and reduction in CH with an increase in take-off angle. The changes in these values are comparable for both SAMs. This illustrates the increased presence of ethylene glycol monomers in the outer surface region and shows little difference between the two types of terminal functional groups. The 40 nm AuNPs show a sightly greater surface OEG concentration than 14 nm AuNPs, possibly indicating a more vertically oriented SAM on the 40 nm AuNPs. FTIR indicates similar crystalline CH2 backbones for all samples, however it appears the structure of OEG head groups are less crystalline on the 14nm AuNPs. This likely results in thicker and/or higher density SAMs on the 40 nm AuNPs compared to the 14nm AuNPs. This is consistent with the nearly identical XPS determined surface elemental compositions determined for OEG SAMs on the two different sized AuNPs. This is contrary to previously XPS results observed for AuNPs functionalized with COOH SAMs [1].

1. Techane, S.D., L.J. Gamble, and D.G. Castner, *Multi-technique Characterization of Self-assembled Carboxylic Acid Terminated Alkanethiol Monolayers on Nanoparticle and Flat Gold Surfaces*. J Phys Chem C Nanomater Interfaces, 2011. **115**(19): p. 9432-9441.

5:40pm **AS+BI-TuA12 Characterization Challenges of Ceria Nanoparticles: When is a Nanoparticle Not a Nanoparticle?**, ***D.R. Baer***, *P. Munusamy, A.S. Karakoti,* EMSL, Pacific Northwest National Laboratory, *S.V.N.T. Kuchibhatla,* Battelle Science and Technology India, *S.S. Seal,* University of Central Florida, *S. Thevuthasan, C.F. Windisch, Jr.*, EMSL, Pacific Northwest National Laboratory

Cerium oxide (ceria) nanoparticles are widely studied for their current and potential use in catalytic, energy, environmental protection and bio-medical applications. The performance of ceria in many of these applications depends on the ability of cerium to switch between +3 and +4 oxidation states. Unfortunately the physical and chemical properties of ceria nanoparticles reported in the literature are often in consistent and at times contradictory. Our research involves examination of the properties of ceria nanoparticles as they apply to materials science research and impact biological systems. We have found that it is possible a obtain what appears to be a self-consistent understanding of these particles by integrating dynamic light scattering, surface potential and UV-Vis adsorption measurements made in solution with *ex situ* x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and transmission electron microscopy (TEM) observations. These measurements have demonstrated that a simple understanding of the chemical state of ceria nanoparticles as dependent on size is not adequate and has led to some of the inconsistent results in the literature. However, Raman and microXRD of wet ceria nanoparticles (pseudo *in situ*) show that the nature of the particles in solution is even more complex than indicated the above measurements. Raman and microXRD measurements indicate that both the chemical state and structure of the smallest nanoparticles can change depending on the nature of the solution. In solutions with low oxygen activity these particles have a ceria structure with cerium in +3 oxidation state while in highly oxidizing conditions the chemical state switches to +4 but the structure can be highly defected (XRD) and appears to be some type of cerium oxy-hydroxide (Raman). The extent of the transformation depends on the size of the particles and appears complete for the smallest particles and partial or possibly not present for larger particles. These measurements demonstrate that the environment, size and time can impact the nature of these particles and that a variety of analysis methods – *in situ* as well as ex situ – are required for comprehensive understanding of ceria nanoparticle behaviors. Acknowledgement - Aspects of the work have been supported by the National Institute of Environmental Health Sciences under grant NIH U19 ES019544. Portions of this work were conducted in the Environmental Molecular Sciences Laboratory, a DOE user facility operated by Pacific Northwest National Laboratory for the Office of Biological and Environmental Research of the DOE.

Biomaterial Interfaces
Room: 23 - Session BI+AS-TuA

Characterization of Biointerfaces
Moderator: L. Meagher, CSIRO Materials Science and Engineering, Australia

2:00pm **BI+AS-TuA1 Surface Characterization Meets Cells and Proteins**, ***B.D. Ratner***, University of Washington **INVITED**

Surfaces such as Ni(100) and Si(100) have been extensively studied and each has been found to be more complicated than simple geometric models would suggest. In this context, consider more mobile surfaces than these precisely defined crystal surfaces that are comprised of 20 amino acids integrated into hundreds of different proteins. Also, these surfaces may contain lipids and complex saccharide structures. It should be apparent that these surfaces can be staggeringly complex, and yet, as with surfaces in general, they efficiently catalyze complex reactions. But they do this at room temperature and atmospheric pressure in a way that makes life possible. For these reasons, the ability to characterize such surfaces will certainly lead to advances in surface design and surface functionality. Tools taken from the "surface science tool chest" can be applied in special ways to complement the tools developed by biologists for molecularly characterizing such surfaces. This talk, primarily focused on electron spectroscopy for chemical analysis (ESCA) and secondary ion mass spectrometry (SIMS), will start with analysis of amino acids and peptides, move to adsorbed protein films and finally consider complex surfaces such as decellularized extracellular matrices and cell monolayers.

2:40pm **BI+AS-TuA3 Using Binary Solvent Mixtures Produces High Graft Density Poly (Ethylene Glycol) Layers**, *A.R. Arcot,* Aalto University, Finland, *S. Zhang, R.L. Meyer, R. Ogaki,* Aarhus University, Denmark, ***P. Kingshott***, Swinburne University of Technology, Australia

The success of PEG based non fouling surfaces depends on several factors such as graft density [1] and nature of head group-substrate interaction. [2] The 'grafting-to' technique though simple, often results in low pinning density when compared to 'grafting-from' technique. [3] This limitation of 'grafting-to' technique can be overcome by grafting under reduced solubility conditions. [4] We demonstrate a simple and versatile way to coat surfaces with PEG at high graft density using binary solvent mixtures, where a poor and a good PEG solvent are mixed with the PEG. The addition of poor solvent decreases the hydrodynamic radius of PEG molecules and hence results in thicker films due to diminished steric repulsion (Supplementary Fig 1a and 1b). The 'good' and 'poor' solvent pair was chosen based on solubility parameter distance calculated from Hanson solubility parameters. [5]

The PEG thiol films on gold formed from acetone-ethanol mixtures were analyzed using x-ray photoelectron spectroscopy (XPS), ellipsometry and atomic force microscopy. The PEG film gets thicker with more ethanol, which is a poorer solvent for PEG (Supplementary table 1). The high resolution sulfur 2p spectra confirmed the absence of precipitate particles. Grafting under high ionic strength conditions used by Kingshott et al. was used as reference for comparison. [4] The PEG thiol films were exposed to fetal bovine serum (FBS) and it was observed that thicker films could resist protein adsorption better than thin films that were formed from high solubility conditions. This method of using binary solvent mixtures can be extended to any polymer-substrate system by choosing appropriate 'good-poor' solvent pair. To demonstrate this point we also studied 5 kDa PEG silane films grafted using acetone-diethyl ether solvent mixture.

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4. P. Kingshott, H. Thissen and H. J. Griesser, Biomaterials (9), 2043-2056 (2002).

5. B. A. Miller-Chou and J. L. Koenig, Progress in Polymer Science (8), 1223-1270 (2003).

3:00pm **BI+AS-TuA4 Adsorption Behavior of Serum Albumin on Nanocrystalline Apatites**, ***K. Fears***, *D. Burden, C. Love,* U.S. Naval Research Laboratory, *D. Day,* Missouri University of Science and Technology, *T. Clark*, U.S. Naval Research Laboratory

The adsorption behavior of bovine serum albumin (BSA) on nano-crystalline hydroxyapatite (HA) and strontium apatite (SrHA) microspheres, derived from borate glasses, was assessed using circular-dichroism spectroscopy (ECD). Numerous reports have shown that surfaces which present nano-sized features can exhibit better cellular response than surfaces with features in the micron regime. The microspheres were incubated in BSA solutions (40 mg/mL; ~64% helix; ~1% sheet) to determine if BSA adsorbed in a fundamentally different manner than on bioinert yttria-alumina-silicate (YAS) spheres that induced minimal conformational changes (~56% helix; ~4% sheet). On the apatite spheres, BSA loss a substantial amount of its helical structure and strained disulfide bonds were detected. However, the protein density on the SrHA spheres was 50% lower than on the HA spheres, indicating that BSA has a higher affinity for irreversible adsorption on HA. 5,5'-Dithio-bis-(2-nitrobenzoic acid), was used to selectively modify free thiols post-adsorption, indicating that solvent-accessible free cysteines were present on the apatite spheres, despite the absence of a reducing agent. Subsequent BSA molecules, or other proteins in vivo, could potentially form intermolecular disulfide bonds leading to increased adhesion of proteins or support the formation of macroscopic protein structures.

4:00pm **BI+AS-TuA7 Quantitative Characterization of Cells in Biofilms and on Surfaces**, *A.C. Areias, C. Sousa, G.P. Mendes,* University of Minho, Portugal, *P. Mack,* Thermo Fisher Scientific, UK, *S. Lanceros-Méndez,* University of Minho, Portugal, ***D.Y. Petrovykh***, International Iberian Nanotechnology Laboratory, Portugal

Films of cells on solid substrates are encountered in a variety of biological and biomedical environments, including cells in biofilms that spontaneously colonize medical devices and multilayers of cells filtered from suspensions for analysis. Understanding the chemical properties of cells in such films is important for providing clues about the behavior of the cells or about the effects of treatments that had been applied to the cells. Similarly to other

types of surface-based systems, the characterization of cells on solid substrates poses several analytical challenges. In particular, the small number of cells on each sample, the interference from surface interactions, and the absorbance of the substrate material prevent the characterization of cells on surfaces by the standard optical methods that are used in solution. We show that protocols similar to those used for preparing samples for electron microscopy can be adapted to prepare biofilm samples for characterization by X-ray photoelectron spectroscopy (XPS). Modern XPS instruments also provide the functionality required for characterization of these complex samples, for example, sample charging on insulating substrates can be efficiently and consistently compensated. Finally, the Ar cluster ion beam technology that recently became available on XPS instruments provides additional capabilities for a more detailed characterization of cells in biofilms, which typically have thicknesses larger than the sampling depth of XPS. We characterized several types of fixed and dried cell samples, including biofilms and cells filtered from suspensions, to compare different preparation protocols and to identify qualitative and quantitative parameters that can be reliably obtained from XPS analysis of such films of cells. We will present the results of our comparative analysis and possible applications of our methodology for characterization of cells in biological and biomedical experiments.

4:20pm **BI+AS-TuA8 Antimicrobial Multilayers and Their Analysis by Laser Desorption Postionization Mass Spectrometry**, *M. Blaze, C. Bhardwaj, A. Akhmetov,* ***L. Hanley***, University of Illinois at Chicago

Bacterial biofilms are structured communities of microbes encapsulated within a self-developed polymeric matrix which adhere to surfaces and display genetic expression distinct from freely floating bacteria. Biofilms are frequently found to populate medical devices, leading to significant problems of infection in the first few days after implantation. Polyelectrolyte multilayers are developed for the delayed delivery of antibiotics to inhibit biofilm growth on biomedical devices [1]. Ten layers each of chitosan and alginate are prepared on a gold substrate, then infused with a novel antibiotic compound. This antibiotic-infused multilayer is found to inhibit the growth of *Enterococcus faecalis* bacterial biofilms on membranes over an 18 hour exposure. Laser desorption postionization mass spectrometry (LDPI-MS) is used to characterize the antibiotic after synthesis [2]. LDPI-MS analysis shows that the antibiotic survives sterilization of the multilayer surface, but <1% of the antibiotic remains after exposure to the biofilm.

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4:40pm **BI+AS-TuA9 Combining Colloidal Probe Atomic Force and Reflection Interference Contrast Microscopy to Study the Mechanics of Biopolymer Films**, ***R.P. Richter***, CIC biomaGUNE, Spain; Joseph Fourier University, France; Max Planck Institute for Intelligent Systems, Germany, *S. Attili,* CIC biomaGUNE, Spain; Max Planck Institute for Intelligent Systems, Germany, *V. Borisov*, Institut Pluridisciplinaire de Recherche sur l'Environnement et les Materiaux, France

Highly solvated polymer films have naturally evolved as multifunctional interfaces in biological systems, e.g. as mucosal films, cellular coats or bacterial biofilms. Surface-confined polymer films are also becoming increasingly popular as biomaterials and in various (bio)technological applications. The mechanical response of such polymer films is not only important for functional performance, but it can also provide valuable information about the film's internal organization, interactions and dynamics.

Here, we present a method that combines colloidal probe atomic force microscopy (AFM) and reflection interference contrast microscopy (RICM) to measure the mechanical properties of thin and solvated polymer films. When analyzing such films, a fundamental problem in colloidal probe AFM experiments is to determine the distance at closest approach between the probe and the substrate on which the film is deposited. By combining AFM and RICM *in situ*, forces and absolute distances can be measured simultaneously, and experimental drifts that otherwise would pass unnoticed can be corrected (1).

We used the combined setup to quantify the compressive mechanics of films of end-grafted hyaluronan (HA brushes) (2). Hyaluronan is a polysaccharide that plays a vital role in the organization and function of pericellular coats and extracellular matrices in vertebrates, and that is also attractive for biomedical applications. We show that HA brushes can swell dramatically as a function of ionic strength or upon binding of the cartilage proteoglycan aggrecan. Detailed comparison of the experimental data with polymer theory reveals that hyaluronan is a prototype of a strongly charged, semiflexible polyelectrolyte with intrinsic excluded volume (3).

The novel combined AFM/RICM setup should be broadly applicable to quantify the mechanical properties of soft hydrated polymer films with precise control of probe-sample separation. The generated data on HA brushes represent a valuable reference for future quantitative studies of more complex HA-rich films and to refine theories of polyelectrolyte brushes of strongly charged and intrinsically stiff polyelectrolytes.

References:

(1) Attili and Richter *Langmuir* **2012,** 28:3206;

(2) Richter et al. *J. Am. Chem. Soc.* **2007,** 129:5306;

(3) Attili et al. *Biomacromolecules* **2012,** in press.

5:00pm **BI+AS-TuA10 Surface Modification of Silicone Hydrogels through Adsorption of Diblock Copolymers**, ***Y.J. Huo***, *S.S. Perry*, University of Florida

The interaction between an ethylene oxide-*block*-butylene oxide (EOBO) copolymer surfactant and the surfaces of four silicone hydrogel (SH) contact lenses—PureVision® (PV), O_2OPTIX® (O_2), ACUVUE® Oasys ® (AO), and Biofinity® (BF)—was investigated using angle-resolved X-ray photoelectron spectroscopy (AR-XPS) following treatment in test solutions containing various concentrations of EOBO. The nature of this interaction was further understood by quantifying the amount of eluted EOBO from each lens following the same treatment using ultra performance liquid chromatography (UPLC). The elution study revealed a large disparity in the amount of EOBO uptake by the different samples following each solution treatment. The XPS results, however, suggested that the amount of EOBO retained on the surface of the lenses demonstrated a largely different trend. For example, AO and BF displayed little evidence of signal at binding energies characteristic of the EO blocks, whereas O_2 and PV exhibited a clear EO signature. The correlation between the elution and XPS results highlights the difference in the interaction mechanism of the EOBO copolymer with different lenses. For lenses such as O_2OPTIX®, this interaction is predominantly bound to the surface; for ACUVUE® OASYS®, however, EOBO was uniformly distributed through the lens structure.

5:20pm **BI+AS-TuA11 Microfluidic Devices for High-Throughput Quantitation in Biology: From Biophysics to Diagnostics**, ***S. Maerkl***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

Microfluidic devices promise to have a significant impact on human health, particularly in diagnostics and drug development. We have developed a suite of microfluidic devices for high-throughput protein biochemistry and applied them to a wide range of applications spanning from protein biophysics to diagnostics, drug development, and vaccine development. Here I will discuss a novel approach to obtaining hundreds of kinetic rate measurements of bimolecular interactions on a single microfluidic device. In a second example I will present a generic microfluidic platform capable of quantitating biomarkers from a wide variety of samples in high-throughput and ultra-low cost, which could ultimately supersede the classical ELISA assay. We applied this platform to vaccine development by quantitating the activation of dendritic cells in response to a large panel of binary adjuvant combinations.

In Situ Microscopy and Spectroscopy Focus Topic
Room: 7 - Session IS+AS+BI+ET+GR+NS-TuA

In Situ Studies of Organic and Soft Materials and In Situ Microscopy

Moderator: K. Artyushkova, The University of New Mexico, J.A. Eastman, Argonne National Laboratory

2:00pm **IS+AS+BI+ET+GR+NS-TuA1 Micronutrient Detection and Quantification from Data Obtained from Plasma Pencil Atmospheric Mass Spectrometry**, ***M.J. Stein***, *E. Lo, C. Waterton, D.G. Castner, B.D. Ratner*, University of Washington

The analysis of micronutrient quantities is one component in the strategy to reduce the global burden of malnutrition-related disease. Accessibility of the proper equipment and equipment complexity impede nutrient testing in the areas that might benefit most from these studies. In this work, we present an analysis of micronutrients in a physiological range from blood plasma using plasma pencil atmospheric mass spectrometry (PPAMS), a method for sampling a sample's surface at ambient temperature and pressure conditions. The effectiveness of our PPAMS system is demonstrated using characteristic and tandem mass spectra on raw nutrient controls. Key micronutrient peaks and fragmentation patterns are observed. Next, we analyze a sample matrix of micronutrients in porcine plasma in

which the nutrient concentrations are varied. Principal component analysis (PCA) is then employed on the spectra. The resulting PCA scores showed that these nutrients are separable at different nutrient concentrations to 95% confidence. The loadings peaks are shown to contain several of the key peaks observed in the raw nutrient powders as principal separators. The PPAMS technique is compared to several traditional techniques such as time-of-flight secondary ion mass spectrometry (ToF-SIMS) and electrospray ionization mass spectrometry (ESI-MS). Separation of the nutrients at concentrations relevant for human blood-based nutrient detection is possible in both ESI-MS and PPAMS. However, ToF-SIMS is found to require 5x to 1000x higher concentrations than PPAMS for folate, vitamin A, and iodine in order to achieve similar separation of the micronutrients. In addition to the qualitative information obtained from the PCA results, quantitative predictive values are obtained by the application of a Bayesian wavelet-based functional mixed model. Since the mass spectra are modeled as functions in this model, peak detection methods are not required and the final results utilized the full spectral response. The final predicted values are compared to the known concentration values and the mean standard error of prediction (MSEP) is calculated. The accuracy of the predictive model was found to be dependent on the ionization potential of the individual nutrients. Metallic-nutrients were hypothesized to be more sensitive to outside cationization effects than their larger organic counterparts. In addition to quantitation, the physical properties of the ionization process were explored. Using XPS and ellipsometry in conjunction with carefully timed exposures and concurrent fragment PCA, it is determined that the PPAMS ionization is a softer form of ionization than most vacuum-based techniques.

2:20pm **IS+AS+BI+ET+GR+NS-TuA2 *In Situ* Real Time Examination of the Thin Film Growth of Pentacene on Polymeric Dielectrics Using X-Ray Synchrotron Radiation: Unexpected Changes in the Evolution of Surface Morphology with Substrate**, *T.V. Desai, A.R. Woll,* ***J.R. Engstrom***, Cornell University

We have examined the thin film growth of pentacene on SiO_2 and on three different polymeric dielectrics using *in situ* synchrotron x-ray scattering and *ex situ* atomic force microscopy (AFM). The polymeric dielectrics investigated spanned the range from a low surface energy hydrophobic surface (polystyrene, PS), to a medium surface energy hydrophobic surface (polymethylmethacrylate, PMMA), to a high surface energy hydrophilic surface [poly(ethylene imine), PEI]. We have also compared these results to pentacene growth on clean SiO_2. On all surfaces, pentacene forms a polycrystalline thin film, whose structure is that of the previously identified "thin film" phase. From *in situ* real-time x-ray scattering, we find that pentacene exhibits layer-by-layer (LbL) growth on all surfaces investigated, but the extent of LbL growth is a strong function of the underlying substrate. This result is unexpected as the transition to more 3D-like growth occurs for thicknesses where the underlying substrate is effectively almost entirely covered by the growing pentacene thin film. Layer-by-layer growth is significantly more prolonged on PEI (up to ~6 MLs), followed by SiO_2 and PMMA (up to ~4 MLs) and finally PS (up to ~ 3 MLs). This trend is also seen in the variation of both the roughness and the in-plane feature sizes of ~ 10 ML thick films, where the films are the smoothest, and the feature sizes are the largest for growth on PEI, whereas on PS, the films are roughest, and the feature sizes are the smallest. Concerning possible reasons for this behavior, we can exclude the effects of the structure of the crystalline thin film (they were the same in all cases), and the roughness of the polymeric dielectric (rms roughness differed by < 0.1 nm) as major contributing factors. Surface energy of the polymeric thin films, however, provided the best explanation for the observed behavior, suggesting that thermodynamic driving forces play an important role in the evolution of thin film structure. In terms of molecular scale phenomena, interlayer transport and step-edge crossing events may be influenced by the mobility of the near-surface polymeric layers in the underlying substrate, which can be quite different for the ultrathin PEI layers vs. the much thicker PMMA and PS thin films.

2:40pm **IS+AS+BI+ET+GR+NS-TuA3 *In Situ*, Real-Time Diagnostics of Colon Cancer and Inflammatory Bowel Diseases by Direct Combination of Endoscopy and Rapid Evaporative Ionization Mass Spectrometry**, ***Z. Takats,*** Imperial College, UK, *L.A. Sasi-Szabo,* University of Debrecen, Hungary, *J. Kinross,* Imperial College, UK, *J. Balog,* Medimass Ltd., *L. Muirhead, K.C. Schafer, C. Guallar-Hoyas*, Imperial College, UK **INVITED**

Rapid identification of biological tissues is a long-standing problem on various fields of interventional medicine, with special regard to cancer diagnostics and cancer surgery. WWhile histological techniques provide the ultimate solution for the cellular-level identification of cancer cells, the approach is extremely complex and time consuming. Nevertheless, accelerated version of histopathology (so-called 'frozen section' method) is widely used for the intraoperative characterization of tissue samples removed from the surgical area. Since frozen section histology is less reliable than the traditional approaches, and the accelerated procedure still takes approx. 30 minutes for a single sample, there has been ongoing research for the development of more accurate and faster methods.

Molecular spectroscopy techniques including IR, Raman, solid state NMR and mass spectrometry have been used for the characterization of intact biological tissues and showed enormous potential for the differentiation of tissues with various histologies, including multiple different types of cancer.

Rapid Evaporative Ionization Mass Spectrometry is based on the observation that electrosurgical dissection of vital tissues involves the ionization of various tissue constituents, with special emphasis on membrane lipids. Electrosurgical methods employ electric current for the rapid heating and evaporation of tissue material and they are widely used both for dissection and coagulation on practically all fields of surgery. Hence, the direct combination of electrosurgery with mass spectrometry provides a tissue identification methodology, where the tissue manipulation part is already widely used by surgeons and fully approved from regulatory point of view. Electrosurgical methods are also employed on the field of endoscopy, both for coagulation and dissection. Combination of endoscopy with in-situ mass spectrometric tissue identification resulted in a diagnostic device which can potentially identify lesions in body cavities in-situ, in real-time.

Electrosurgical electrode assembly and ion transfer device were embedded into working channel of commercially available colonoscope. The device was coupled with a linear ion trap mass spectrometer, and the system was utilized during diagnostic colonoscopic interventions. Adenomae, adenocarcinomae and mucosal areas affected by inflammatory bowel diseases were successfully identified, in complete agreement with histopathological examination.

4:00pm **IS+AS+BI+ET+GR+NS-TuA7 Nanocrystal Phase Transformations in ZBLAN Glass Ceramics**, ***J.A. Johnson,*** University of Tennessee Space Institute, *C. Alvarez,* Northwestern University, *Y. Lui,* Argonne National Laboratory, *C.E. Johnson,* University of Tennessee Space Institute, *A. Petford-Long*, Argonne National Laboratory

In-situ and *ex-situ* TEM investigations of fluorochlorozirconate (FCZ) glass have led to the discovery of previously unreported BaF2 in the face-centered-cubic (FCC) and orthorhombic phases. These FCZ glasses are a class of material based on ZBLAN glasses, which are being developed for uses in advance mammography systems. The FCZs of interest have been doped with Eu (II) for use as either a scintillator or a storage phosphor material but need to be partially crystalline to show good optical properties. The photo-stimulated luminescence of this material, for use as storage phosphor, is attributed to the characteristic 5d-4f emission of Eu2+ present in the BaCl2 nanocrystals. The crystals formed are known from XRD experiments to be hexagonal and orthorhombic BaCl2 depending on the annealing temperature, 265 and 295°C respectively. *In-situ* and *ex-situ*TEM heating experiments were used to study the nucleation and growth process of the nanocrystals at the EMC. The nanocrystals nucleate and grow through-out the glass matrix when annealing FCZ glasses, therein producing a nanocomposite glass-ceramic system. The traditional BaCl2 orthogonal phase in addition to the unreported FCC and orthogonal BaF2 phase have been found in multiple ZBLAN compositions in which the content of Cl and F has been varied. This indicates that annealing FCZ glasses produces polymorphic crystals of both BaCl2 and BaF2, which vary in size from 10 nm to 100 nm.

Mössbauer Spectroscopy has also given indisputable evidence that the divalent Europium enters the nanocrystals.

4:20pm **IS+AS+BI+ET+GR+NS-TuA8 *In Situ* Microscopy of Organic Film Growth: Zn-Phthalocyanine on Ag(100)**, ***A. Al-Mahboob***, *J.T. Sadowski*, Brookhaven National Laboratory

Metal phthalocyanines are attracting significant attention, owing to their potential for applications in chemical sensors, solar cells and organic magnets. As the electronic properties of molecular films are related to their crystallinity and molecular packing, the optimization of film quality is important for improving the performance of organic devices.

In this work, we studied the dynamics of nucleation and structural evolution of zinc-phthalocyanine (ZnPc) films on Ag(100) surface, employing real-time low-energy electron microscope (LEEM) complemented by DFT calculations. We have observed two different modes of ZnPc nucleation, depending on the growth temperature. At lower temperatures ZnPc nucleates in a double domain structure, with bulk-like square lattice similar to one reported by Dou et al. [2]. LEED patterns recorded in LEEM experiment show that ZnPc monolayer (ML) grows epitaxially, having a square lattice with $(4/3)\sqrt{(13)}$x$(4/3)\sqrt{(13)}$R33.69° unit cell (denoted R33.69) with respect to the substrate lattice. At temperatures of 170°C or above, nucleation of less dense epitaxial ZnPc, having single domain orientation,

was observed, with square lattice parameters exactly 5 times larger (5x5) than the Ag(100) substrate.

Utilizing LEEM to observe the ZnPc nucleation at varying substrate temperatures – from room temperature (RT) to 225°C – we have observed that the nominal ZnPc coverage required for the onset of nucleation has strong temperature dependence. The nucleation commences at about 0.2 ML at RT, while 0.7 ML is required at 190°C. At the same time the completion of 1st layer occurs at constant nominal coverage of ZnPc, independent of substrate temperature. Based on that observation, the delay in onset of nucleation could be understood as a result of increased equilibrium concentration of diffusing ZnPc molecules at higher temperatures. This is in contrast to a delay in nucleation and giant island growth observed during vacuum deposition of anisotropic molecules like pentacene (Pn), in which case the energy barrier for the reorientation of the molecule from diffusing state into its crystalline orientation plays a critical role [3]. Real-time tracking of the evolution of ZnPc island area at varying deposition conditions combined with DFT analysis revealed that the 5x5 structure has both, a detachment barrier with respect to attachment, and a pre-factor (or attempt frequency), lower than those for bulk-like structures, allowing for controlling of the resulting ZnPc structure.

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4:40pm **IS+AS+BI+ET+GR+NS-TuA9 *In Situ* Sub-Micrometer Scale Chemical Imaging with Scanning Transmission X-ray Microscopy**, ***S.T. Kelly***, *P. Nigge,* Lawrence Berkeley National Laboratory*, A. Laskin, B. Wang,* Pacific Northwest National Laboratory*, A. Tivanski, S. Ghorai,* University of Iowa*, T. Tyliszczak, M.K. Gilles*, Lawrence Berkeley National Laboratory

Spatially resolved chemical information on length scales shorter than 50 nm has become crucial in many areas of science and engineering -- from analyzing the chemistry of geological and environmental samples to quantifying the detailed chemical structure of novel materials engineered on the nanoscale. Scanning transmission x-ray microscopy (STXM) allows collection of specific chemical speciation data on these length scales through the acquisition and analysis of near-edge x-ray absorption fine structure (NEXAFS) spectra at each image pixel. However, the full usefulness of the STXM instrument may ultimately be realized in the in situ analysis of chemical transformations by controlling the local sample environment.

In situ STXM/NEXAFS measurements have been made in several ways thus far, ranging from simple to very complex. Introducing gases directly into the microscope chamber is effective, yet the presence of the gas along the entire optical path of the x-rays reduces signal at the detector. Furthermore, gas choice with this configuration is limited to those compatible with the microscope components. Separate in situ reactor cells circumvent these limitations by confining the gaseous environment to a small region immediately around the sample. Several groups have used reactor cells to this end, with reactors ranging widely in complexity -- from simple cells with limited capability to complex systems which require substantial instrument reconfiguration.

Ideally, an in situ reactor for STXM should be capable, flexible, easy to install and configure, and easily fabricated. We have developed a gas phase STXM reactor cell to meet many of these requirements. The reactor mounts directly to the standard STXM sample mount (making installation relatively simple) and contains an integrated sensor to actively measure relative humidity inside the cell for experiments using water vapor. We present here recent results using the reactor cell to examine two different systems. In the first system, we observed the hygroscopic properties of mixed organic/inorganic aerosol particles at increasing levels of relative humidity. In the second system, we monitored carbon dioxide sorption in metal organic framework materials. The advantages afforded by this reactor (and future improvements to it) will enable new scientific discoveries across a wide range of fields.

5:40pm **IS+AS+BI+ET+GR+NS-TuA12 *In Situ* SEM and ToF-SIMS Imaging of Liquids for Biological Applications**, ***L. Yang***, *X.-Y. Yu, Z. Zhu, S. Thevuthasan,* Pacific Northwest National Laboratory*, J. Cowin*, Cowin In-Situ Science, L. L. C.

A vacuum compatible microfluidic interface was developed to enable surface analysis of liquids. The unique feature of the liquid flow cell is that the detection window is open to the vacuum allowing direct probing of the liquid surface. The flow cell is composed of a silicon nitride membrane and polydimethylsiloxane; and it is fully compatible with vacuum operations for surface analysis. The aperture can be drilled through the 100 nm silicon nitride membrane by using the focused ion beam/scanning electron microscope (FIB/SEM). Alternatively the primary Bi^+ ions in ToF-SIMS can be used to fabricate the aperture window in real-time. New results using this vacuum interface and recent development will be presented in this paper. Several aqueous solutions containing conjugated IgG gold nanoparticles and representative biological solutions were studied *in situ* using scanning electron microscope (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS). Characteristic signals of the conjugated gold nanoparticles were successfully observed through the aperture by both energy-dispersive X-ray spectroscopy (EDX) in SEM and ToF-SIMS. Comparisons were also made among wet and dry samples and liquid sample in the flow cell using SEM/EDX. Stronger gold signal can be observed in our novel portable device by SEM/EDX compared with the wet or dry samples, respectively. Our results indicate that analyses of the nanoparticle conjugated antibodies are better made in their native liquid environment. Our unique microfluidic flow cell permits *in situ* liquid observations. In addition, a variety of aqueous solutions relevant to biological systems were analyzed. Our results indicate that chemical imaging by SEM and ToF-SIMS is applicable in analyzing more complicated aqueous solutions when coupled with our novel portable microfluidic platform.

Magnetic Interfaces and Nanostructures
Room: 6 - Session MI+EN+BI-TuA

Fundamental Problems in Magnetism
Moderator: G.J. Szulczewski, The University of Alabama

2:00pm **MI+EN+BI-TuA1 Spintronics – Implications for Energy, Information and Medical Technologies**, ***S.D. Bader***, Argonne National Laboratory and Northwestern University **INVITED**

Spintronics encompasses the ever-evolving field of magnetic electronics.[1,2] Fields such as spintronics are hold the potential to extend the information technology revolution as the semiconductor road map reaches its end . A major issue with present day electronics is in its demand for increased power. Spintronics offers the possibility to communicate via pure spin currents as opposed to electric charge currents. The talk provides a brief perspective of recent developments to switch magnetic moments by spin-polarized currents, electric fields and photonic fields. Developments in the field of spintronics continue to be strongly dependent on the exploration and discovery of novel nanostructured materials and configurations. An array of exotic transport effects dependent on the interplay between spin and charge currents have been explored theoretically and experimentally in recent years. The talk highlights select promising areas for future investigation, and, features recent work at Argonne, [3,4] including, most strikingly, in the realm of medical applications. [5]

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Samuel D. Bader, Materials Science Division and Center for Nanoscale Materials, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60208 USA

2:40pm **MI+EN+BI-TuA3 Multiscale Modeling for Spintronics**, ***K.A. Mewes***, *T. Mewes, W.H. Butler*, University of Alabama **INVITED**

The next generation of spintronic devices relies strongly on the development of new materials with high spin polarization, optimized intrinsic damping and tunable magnetic anisotropy. Therefore technological progress in this area depends heavily on the successful search for new materials as well as on a deeper understanding of the fundamental mechanisms of the spin polarization, the damping and the magnetic anisotropy. My talk will focus on different aspects of materials with high spin polarization, low intrinsic relaxation rate and perpendicular anisotropy. Our results are based on first principles calculations in combination with a non-orthogonal tight-binding model to predict those material properties for complex materials which can be used for example in new spin based memory devices or logic devices. Future progress in spintronics not only requires a better understanding of the underlying physical principles but also hinges strongly on the development of theoretical models capable of

describing the expected performance of realistic device structures. As an example I will discuss the challenges in the Spin Transfer Torque Random Access Memory. This memory is dense, fast and nonvolatile and has the capability of a universal memory possibly even replacing today's Dynamic Random Access Memory (DRAM).

4:00pm **MI+EN+BI-TuA7 Anomalous Magneto Transport in Amorphous TbFeCo Film with Perpendicular Magnetic Anisotropy**, ***N. Anuniwat***, *M. Ding, J. Poon, S.A. Wolf, J.W. Lu*, University of Virginia

TbFeCo has attracted some interests because of its high perpendicular anisotropy and tunable magnetic properties for nanomagnetic and spintronics application. Due to the fact that electronic device is getting smaller, fundamental understanding of size and geometry dependent is crucial . In this study, we report a strong size dependence of the coercive field in 15 - 100nm thick Tb30Fe63.5Co6.5 films with MgO capping. Magneto Optical Kerr effect (MOKE) and Vibrating Sample Magnetometer are performed on unpatterned films. The films exhibited strong PMA characteristics. The films were then fabricated into Hall bars with 10 μm, 50 μm, 100 μm and 500 μm in width. From anomalous Hall effect (AHE), HC was determined for these patterned films. We observed coercivity enhancement as the width of the hall bar decreases (up to 200% at room temperature). The temperature dependent of the coercivity is also studied. There exhibits the local minimum as the temperature change from 50 - 300K. The correlation between HCmin and dimensions of the hall bar are discussed. The magnetic domain structures and surface morphology analysis were performed using magnetic force microscopy and atomic force microscopy respectively. The variation in domain sizes , structures for different hall bars as well as possible origins of the coercivity enhancement are also discussed.

4:20pm **MI+EN+BI-TuA8 Magnetic Properties of Fe Clusters: A DFT+U vs Nano DFT+DMFT Analysis**, ***A.K. Kabir***, *V. Turkowski, T.S. Rahman*, University of Central Florida

We use our recently proposed combined density-functional-theory/dynamical-mean-field-theory (DFT + DMFT) approach for molecules and nanosystems [1] to study the magnetic properties of Fe clusters consisting of 15, 17 and 19 atoms. This method has several advantages compared with the widely-used DFT + U approach for systems with localized electron states, the most important of which is that it takes into account dynamical correlation effects. These effects are especially important in the case when the kinetic (hopping) and the local Coulomb repulsion energies have the same order of magnitude. In particular, we study the size-dependence of the magnetic properties of the clusters by using the nanoDMFT code developed in our group using the iterated-perturbation theory approximation in the impurity solver. We find that the DFT+DMFT approach yields much better agreement for the magnetization with experimental data as compared to DFT and DFT+U methods, both of which generally overestimate the magnetization.

Work supported in part by DOE Grant No. DOE-DE-FG02-07ER46354

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4:40pm **MI+EN+BI-TuA9 Rationally-designed Iron Oxide Nanostructures for Bioimaging**, ***Y. Bao***, The University of Alabama **INVITED**

Iron oxide nanoparticles have been extensively studied in targeted delivery, localized therapy, and as contrast agents for magnetic resonance imaging (MRI). In fact, sugar coated iron oxide NPs have been clinically used as the liver/spleen-specific contrast agents in MRI, indicating the biocompatibility and potential of iron oxide nanoparticles in nanomedicine. This presentation will discuss how rationally designed iron oxide nanoparticles can achieve highly effective MRI contrast agents. The talk will primarily focus on the shape control of iron oxide nanoparticles and the surface functionalization. The formation and magnetic properties of various shaped-iron oxides (e.g., cubes, nanoworms, nanoplates, and nanowires) will be elaborated. In particular, ultrathin iron oxide nanowires will be discussed in details, such as synthesis, property, and their potential as MRI contrast agents.

5:40pm **MI+EN+BI-TuA12 3D Vector Magnetometry of Thin-Films using Generalized Magneto-Optical Ellipsometry (GME)**, ***J.A. Arregi***, *J.B. González-Díaz, O. Idigoras, A. Berger*, CIC nanoGUNE Consolider, Spain

Generalized Magneto-Optical Ellipsometry (GME) has emerged in the last decade as a methodology to characterize magnetic materials with a high degree of precision, by means of utilizing the magneto-optical Kerr effect [1]. Compared to other magneto-optical characterization methods based on the same effect, GME has two key advantages: it can measure both the optical and magneto-optical constants, and it allows full vector magnetometry, all with one simple experimental set-up. The technique has been successfully employed in the study of diverse magnetization reversal processes, for the purpose of identifying spin-polarized electronic states in multiferroic materials [2], as well as for the measurement of the magnetization orientation using 2D vector magnetometry [3].

Even if some works have suggested the possibility to perform quantitative 3D vector magnetometry using the GME technique [4], actual measurements have not been demonstrated so far. Here, we extract the field dependent evolution of the three magnetization components during the reversal process. In order to do so, we exploit the different symmetries of the longitudinal, transverse and polar Kerr effect around different polarizer/analyzer crossing points, which allows us to separate the information of each of the magnetically induced contributions to the non-diagonal reflection matrix elements. By combining the presence of in-plane uniaxial anisotropy as well as out-of-plane applied magnetic fields in our Co and Co-alloy based thin films, we manage to monitor the evolution of the full magnetization vector as a function of the field.

In addition to this full vector magnetometry capability, we have recently improved this technique to enhance measurement reliability [5] and we also extended its capabilities to characterize materials that are magneto-optically active and optically anisotropic at the same time [6].

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Scanning Probe Microscopy Focus Topic
Room: 16 - Session SP+AS+BI+ET+MI+NS-TuA

Advances in Scanning Probe Imaging

Moderator: S. Allen, The University of Nottingham, UK, Z. Gai, Oak Ridge National Laboratory

2:00pm **SP+AS+BI+ET+MI+NS-TuA1 Molecules Investigated with Atomic Resolution using Scanning Probe Microscopy with Functionalized Tips**, ***L. Gross***, *F. Mohn, N. Moll, G. Meyer*, IBM Research - Zurich, Switzerland **INVITED**

Single organic molecules were investigated using scanning tunnelling microscopy (STM), noncontact atomic force microscopy (NC-AFM), and Kelvin probe force microscopy (KPFM). With all of these techniques submolecular resolution was obtained due to tip functionalization by atomic manipulation. The techniques yield complementary information regarding the molecular structural and electronic properties.

Using NC-AFM with CO terminated tips, atomic resolution on molecules has been demonstrated and the contrast mechanism was assigned to the Pauli repulsion [1]. On the other hand, by using STM the molecular frontier orbitals, i.e., the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO), were mapped [2]. Using a CO terminated tip for orbital imaging with the STM, the resolution can be increased and the images correspond to the gradient of the molecular orbitals due to the *p*-wave character of the tip states [3]. Finally, KPFM reveals information about the distribution of charges within molecules by measuring the *z*-component of the electrostatic field above the molecule, as demonstrated on the hydrogen tautomerization switch naphthalocyanine [4].

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2:40pm **SP+AS+BI+ET+MI+NS-TuA3 Functional Imaging of Jahn-Teller Dynamics at the Single-molecule Scale**, ***J. Lee***, *S.M. Perdue, A. Rodriguez Perez, P.Z. El-Khoury, V.A. Apkarian*, University of California, Irvine

Taking advantage of both elastic and inelastic tunneling processes of a molecule isolated at the double-barrier tunneling junction of a scanning tunneling microscope, both static and dynamic parts of the Hamiltonian can

be visualized with submolecular resolution. This is illustrated by imaging Jahn-Teller (JT) driven vibronic dynamics within Zn-etioporphyrin (ZnEtio), in its various reduced forms, in what may be regarded as nature's choice of a molecule as a controllable current switch. Unique interpretations are afforded through simultaneously recorded functional images, such as maps of: a) energy resolved differential current, b) spectrally resolved electroluminescence, c) conduction bistability, d) reduction/oxidation potentials (maps of charging and discharging). We focus on the radical anion, $ZnEtio^-$, which is reduced by injecting an electron to a single ZnEtio molecule adsorbed on a thin aluminum oxide film grown on NiAl(110). In contrast with the neutral, the saddle-shaped radical anion lies flat on the surface of the oxide. The discharge map directly shows that the excess electron is localized in the ^2p_x orbital of the entire porphyrin macrocycle, as a result of the JT active rectangular (B_{1g}) distortion of the molecule. The static JT potential leads to conduction bistability, with reversed switching polarity depending on whether tunneling electrons are injected in the occupied ^2p_x orbital or the diamond (B_{2g}) coordinate which serves as a transition state that connects the p_x and p_y orbitals at the two B_{1g} minima. In addition to the JT switching, the dynamic JT states are directly imaged through electroluminescence spectra, induced by injection of a second electron in the anion. The spectra consist of a continuum due to radiative ionization of the dianion, and sharp Fano resonances of the vibronic progression of the JT active modes. A detailed analysis of the spectra yields the vibronic couplings and the wavefunctions. Vibronic structure is inherent in STM topographic images, and has hitherto not been fully recognized.

3:00pm **SP+AS+BI+ET+MI+NS-TuA4 Atomic and Chemical Resolution of Heterogeneous 1-D Metallic Chains on Si(100) by Means of nc-AFM and DFT**, *M. Setvin,* ***M. Ondracek****, P. Mutombo, Z. Majzik, P. Jelinek*, Institute of Physics of ASCR, Czech Republic

Scanning Probe techniques are widely used to image atomic and electronic structure of surfaces and nanostructures. However atomic and chemical resolution of complex nanostructures (e.g. molecules, nanoparticles or nanowires) is still the large challenge. Several methods (see e.g. [1-3]) have been already proposed to achieve the single-atom chemical resolution. In the work [3] it was showed that the single-atom chemical identification can be achieved via force-site spectroscopy measurements using Frequency Modulation Atomic Force Microscopy (FM-AFM). The validity of the method was demonstrated on semiconductor surface alloy composed of isovalent species (Si, Sn and Pb). In this particular case, the valence electrons of surface atoms possess very similar electronic structure close to sp^3 hybridization with characteristic dangling bond state. Hence the maximum short-range force is mainly driven by the position of the dangling bond state with respect to the Fermi level.

In this work, we investigated atomic and chemical structure of heterogeneous 1-D chains made of III and IV group metals grown on Si(100) surface [4] by means of room-temperature (RT) FM-AFM measurements combined with DFT simulations. Here 1D chains consist of heterogeneous buckled-dimer structures with unknown chemical ordering. What more, the presence of buckled dimmers composed by chemical species of different valence makes this system very challenging for true atomic and chemical resolution by means of SPM.

In this contribution, we will show first that FM-AFM technique even at RT is able to achieve atomic resolution of individual atoms forming dimmer-rows, much superior to the contrast obtained by the traditional STM technique. Secondly, we will demonstrate that the single-atom chemical identification is still possible combining the force-site spectroscopy at RT with DFT simulations even in such complex systems as the heterogeneous 1D metallic chains.

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4:00pm **SP+AS+BI+ET+MI+NS-TuA7 Simple Routes to High Speed and Super Resolution AFM**, ***J.K. Hobbs***, University of Sheffield, UK **INVITED**

Over the past two decades atomic force microscopy has developed to become the workhorse of molecular nanotechnology. However, despite this success, it has failed to deliver consistently in two areas where it arguably has most potential, namely sub-molecular resolution imaging and the following of processes in real time. Here our work to tackle these challenges will be discussed.

We have developed a new approach to reaching high resolution within a conventional AFM, based on torsionally driven T-shaped cantilevers, dubbed "torsional tapping AFM". The use of torsional oscillations gives improved dynamics (high Q-factor, high frequency), without excessively increasing the spring constant. The small offset of the tip from the axis of rotation gives improved lever sensitivity. Combined, these result in an approximately 12 fold improvement in sensitivity when compared to the same AFM with a conventional tapping cantilever. This improved sensitivity allows ultra-sharp whisker tips to be used in a routine manner, giving true molecular resolution even on soft materials presenting surfaces with tens of nanometres of topography. For example, individual polyethylene chains both in the crystalline phase, and at the interface with the amorphous phase, can be clearly imaged in a conventionally processed sample of plastic, with polymer chain-to-chain resolution down to 0.37 nm [1]. Data from semi-crystalline polymers to naturally occurring protein crystals will be presented.

High speed AFM requires methods for scanning rapidly, for maintaining tip-sample contact ("feedback"), and for constructing the topography image. We have shown that resonant scanners [2] give a robust method for rapid scanning. In a conventional AFM the feedback and the topographic image are inextricably linked. However, this places a limit on scan speed as it demands that the tip has reached equilibrium at each point on the image if the height is going to be accurately obtained. We have adopted a different approach, in which the height of the tip is directly measured using an interferometric approach, freeing the feedback loop to minimising tip-sample forces. This allows topographic images with height traceable to the wavelength of the interferometric laser to be obtained at imaging rates greater than one frame a second. Coupled with resonant scanners, giving scan areas up to 40×40 um^2 an AFM platform capable of in-line industrial applications is obtained.

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4:40pm **SP+AS+BI+ET+MI+NS-TuA9 A Scanning Probe Microscopy Study of Trimesic Acid Self-Assembly on Highly Oriented Pyrolytic Graphite**, ***V. Korolkov****, S. Allen, C.J. Roberts, S.J.B. Tendler*, The University of Nottingham, UK

We have investigated trimesic acid (1,3,5-benzenetricarboxylic acid, TMA) adsorption on highly oriented pyrolytic graphite (HOPG) surfaces from aqueous medium at room temperature. Both atomic force (Peak Force Tapping mode) and scanning tunnelling microscopy were utilized to follow the adsorption dynamics and molecular arrangements. A chicken-wire arrangement for adsorbed molecules with an average pore size of 11 ± 1Å was established and observed using both scanning techniques. We found that this structure forms a monolayer within ~ 100 seconds of exposure of the HOPG surface to 50μM TMA solution in H2O. The monolayer structure was found to be stable for at least 48h under ambient conditions. STM was observed to lead to some desorption of TMA from a dynamically formed TMA film, and was only able to image the monolayer of TMA molecules in intimate contact with the HOPG. AFM revealed that TMA films formed using higher concentrations or longer adsorption times formed multilayers with similar molecular spacings and displayed an island growth morphology.

We have achieved an excellent resolution on an ambient running AFM. We have demonstrated that the combination of STM and AFM is essential, if not a must, to look at ultimate monolayers in the ambient conditions. Overall a facile green chemistry method for TMA monolayer fabrication from aqueous media on a HOPG surface has been established.

5:00pm **SP+AS+BI+ET+MI+NS-TuA10 Understanding the Role of the Probe in SPM Imaging of Metal Oxides: New Opportunities for In-Depth Surface Analysis**, *H. Mönig,* Univ. of Münster, Germany*, M. Todorovic,* Univ. Autónoma de Madrid, Spain*, M.Z. Baykara,* Yale Univ.*, T.C. Schwendemann,* Southern Connecticut State Univ.*, J. Götzen, Ö. Ünverdi, E.I. Altman,* Yale Univ.*, R. Perez,* Univ. Autonoma de Madrid, Spain*,* ***U.D. Schwarz***, Yale Univ.

Metal oxide surfaces play an indispensible role in a number of catalytic processes of technological and scientific importance. A fundamental understanding of the role that metal oxide surfaces play in such applications requires an experimental technique that allows analyzing chemical and electronic surface properties down to the atomic scale. The powerful method of three-dimensional atomic force microscopy (3D-AFM) in combination with scanning tunneling microscopy (STM) can be used towards this goal with great success. However the interpretation of results is not straightforward, particularly because the structure and chemistry of the probe tip employed in the experiments influences the measured data.

In this talk, using a combination of experimental STM data and density functional theory (DFT) calculations, we will study the effect of changing the tip structure and chemistry, as well as imaging parameters such as tip-sample distance and bias voltage on STM images obtained on the model surface of Cu(100)-O, a surface oxide layer consisting of nearly co-planar

copper (Cu) and oxygen (O) atoms. We observe that STM image contrasts and atomic species with highest tunneling probability vary greatly with changing tip properties and imaging parameters. Reasonable matches between calculated and experimentally recorded STM images are observed, allowing the determination of particular tip models used in the experiments. Additionally, the effect of rotating the model tip structures with respect to the sample surface results in asymmetric features in simulated STM images, reproducing certain peculiar patterns observed experimentally. To sum up, the results presented here underline the significant role that the tip plays in SPM measurements and describe potential routes to optimize the gathered information through deliberate manipulation of tip properties as well as imaging parameters.

5:20pm **SP+AS+BI+ET+MI+NS-TuA11 Characterizing the Best Tips for NC-AFM Imaging on Metal Oxides with Force Spectroscopy and Theoretical Simulations**, *D. Fernandez-Torre,* Universidad Autónoma de Madrid, Spain, *A. Yurtsever,* Osaka University, Japan, *P. Pou,* Universidad Autónoma de Madrid, Spain, *Y. Sugimoto, M. Abe, S. Morita,* Osaka University, Japan, ***R. Perez***, Universidad Autónoma de Madrid, Spain

Metal oxides play a key role in a wide range of technological applications. To optimize their performance, it is essential to understand their surface properties and chemistry in detail. Noncontact atomic force microscopy (nc-AFM) provides a natural tool for atomic-scale imaging of these insulating materials. Some of these materials, including ceria (CeO2), and particularly titania (TiO2), have been extensively studied with nc-AFM in the last few years. Experiments on the rutile TiO2(110) surface show, at variance with STM, that a variety of different contrasts can be obtained, and frequent changes among different imaging modes are observed during scanning. The two most common contrasts are the "protrusion" and the "hole" mode imaging modes, that correspond, to imaging bright the positive or the negative surface ions respectively, but other contrasts like the "neutral" mode and the "all-inclusive" mode –where all the different chemical species and defects are imaged simultaneously—have been also identified.

Understanding the image contrast mechanisms and characterizing the associated tip structures is crucial to extract quantitative information from nc-AFM measurements and to identify the nature of the observed defects. While in many cases the same nc-AFM image can be explained by different models, and even different underlying tip-sample interactions, we show here that the combination of force spectroscopy (FS) measurements and first-principles simulations can provide an unambiguous identification of the tip structure and the image contrast mechanism. In particular, we show that the best tips to explain the protrusion and hole mode forces are TiOx-based clusters differing in just one H atom at the tip apex, discarding previously proposed Ti-terminated tips that would lead to forces much larger than the ones observed in the experiments. The less frequent neutral and all-inclusive images are associated to Si tips where contamination is limited to just an O atom or OH group at the apex. These models provide a natural explanation for the observed contrast reversals by means of H transfer to/from the tip, an event that we indeed observe in our simulations. As tip contamination by surface material is common while imaging oxides, we expect these tips and imaging mechanisms to be valid for other oxides. Our results for the imaging of CeO2 surfaces and of metal atoms (K, Pt) adsorbed on TiO2 support this conclusion.

5:40pm **SP+AS+BI+ET+MI+NS-TuA12 Direct Probe of Interplay between Local Structure and Superconductivity in $FeTe_{0.55}Se_{0.45}$**, ***M.H. Pan***, *W.Z. Lin, Q. Li, B.C. Sales, S. Jesse, A.S. Sefat, S.V. Kalinin*, Oak Ridge National Laboratory

A key challenge in high-temperature superconductivity is to determine the role of local crystallographic structure and chemical effects on the superconducting critical temperature, T_c . Iron chalcogenide superconductors ('11') are ideal model systems for deciphering the role of local effects on the superconductivity, primarily because they cleave leaving non-polar surfaces unlike other families of iron arsenide superconductors ('1111' or '122') and cuprates . **Here, we explore the interplay between local crystallographic structure, composition and local electronic and superconductive properties. Direct structural analysis of scanning tunneling microscopy (STM) data allows local lattice distortions and structural defects across a $FeTe_{0.55}Se_{0.45}$ surface to be explored on a single unit-cell level. Concurrent superconducting gap (SG) mapping reveals suppression of the SG at well-defined structural defects, identified as a local structural distortion (Guinier-Preston zone). The strong structural distortion is related to the vanishing of the superconducting state. This study provides insight into the origins of superconductivity in iron chalcogenides by providing an example of atomic-level studies of the structure-property relationship.**

Biomaterial Interfaces
Room: Central Hall - Session BI-TuP

Biomaterial Interfaces Poster Session

BI-TuP1 Response of Mesenchymal Stem Cells to Nano-Scale Rippled Silicon Surfaces, *O.Z. Andersen, A. Keller, D.C.E. Kraft, F. Besenbacher,* ***M. Foss***, Aarhus University, Denmark

Proliferation of stem cells has been observed to be affected by surface roughness in the micro and nanometer range. Furthermore, when cultured on line patterns with dimensions in the sub-micrometer regime these have been found to adopt elongated morphologies and align with respect to patterns, often called contact guidance. Contact guidance has been observed to induce stem cell differentiation towards neurogenic and myogenic lineages. We have investigated the effect of rippled silicon substrates with different height and periodicity in the nanometer range on the behavior of human derived adult stem cells.

The substrates were prepared by irradiating silicon substrates with xenon ions with different energies and fluxes at angles of either 65 or 67º with respect to the surface normal. From this, substrates with nanoripples of different heights (h) and periodicities (λ) were obtained. As determined by AFM measurements the prepared substrates had ripple features ranging from h=3 nm with λ=50 nm up to h=70 nm with λ=650 nm. The cellular response towards these surfaces was investigated using human dental pulp stem cells (hDPSC). The cells (2,500 cell/cm^2) were cultured for periods of 1, 3 and 4 days, fixed and used for assessing cellular proliferation, morphology, alignment with respect to the ripple structures and expression of the osteogenic markers Runx2 and ALPL and the myogenic markers GATA4 and MyoD1.

It is found that the ripple structures influenced cellular proliferation. An increase in proliferation was observed up until ripple structures with h=8 nm and λ=170 nm followed by a decrease as the ripples structures further increased in size. The decrease in proliferation for larger ripple structures was found to correlate with an increasing number of cells undergoing contact guidance. Furthermore, it was found that the cells cultured on the ripple surfaces with features larger than h=8 nm and λ=170 nm had up-regulated expression of the myogenic markers.

The increasing ripple size is associated with larger RMS roughness values. Hence, the increase in cellular proliferation as the ripples grows in size, correlate well with literature on cellular behavior on rough samples. The decrease in proliferation observed with the larger ripple structures correlates with the increasing degree of contact guidance observed for these samples. We speculate that it could be related to changes in the cellular expression profiles. This is supported by the data from the immunohistochemistry. Especially the finding that the expression of MyoD1 is up-regulated with the larger ripple structures as this regulatory protein is known to be associated with cell cycle arrest.

BI-TuP2 *In Vitro* Cytotoxicity of Poly(*N*-isopropyl acrylamide), ***M.A. Cooperstein***, *H.E. Canavan*, University of New Mexico

Poly(*N*-isopropyl acrylamide) (pNIPAM) is a thermoresponsive polymer that undergoes a conformation change in a physiologically relevant temperature range. Above its lower critical solution temperature (LCST, ~32°C), pNIPAM is relatively hydrophobic, and cells can be easily cultured on pNIPAM-grafted surfaces. When the temperature is lowered, the polymer's chains extend and cells detach in intact sheets. It has previously been demonstrated that the NIPAM monomer is toxic; however, there are conflicting opinions as to whether the polymerized form of NIPAM is toxic. Since the cell sheets detached from pNIPAM could ultimately be used on humans, it is crucial to assess the cytotoxicity of surfaces coated with pNIPAM. Very few (<10) studies exist that investigate the cytotoxicity of pNIPAM, and their results are conflicting. Furthermore, the published studies are not comprehensive. Instead, they focus on isolated cell lines cultured on pNIPAM films generated using different methods, and use different assays to determine the degree of cytotoxicity. In this work, we present a comprehensive investigation of the cytotoxicity of pNIPAM-grafted surfaces. The cytotoxicity of pNIPAM is evaluated using different cell lines (endothelial, epithelial, smooth muscle, and fibroblasts), polymerization (free radical and commercially available pNIPAM) and deposition (spin coating and plasma polymerization) techniques, and cytotoxicity tests (MTS, Live/Dead, plating efficiency). The pNIPAM-coated surfaces are evaluated using X-ray photoelectron spectroscopy and goniometry. We find that there is lower cell viability on pNIPAM surfaces when compared to controls. The viability also seems to be deposition type dependent. 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.

BI-TuP3 Functionalization of Cerium Oxide Nanoparticles with Biocompatible Molecules to Prevent Surface Modification by Phosphate Ions, ***P. Mendez***, *S. Das, A. Kumar, S. Sudipta*, University of Central Florida

Cerium oxide nanoparticles (CNP's) are a promising catalytic antioxidant in biological systems, exhibiting superoxide dismutase and catalase mimetic, and nitric oxide radical scavenging activity. Nanoceria exhibits redox activity by switching between Ce 3+ and 4+ depending on environment. CNPs have also been shown to protect cells against oxidative stress. Specific formulation of cerium oxide nanoparticle is non-toxic, non-immunogenic and well tolerated both *in vitro* and *in vivo* model, which provide the rational/platform for its biological applications. Recently CNPs have become increasingly popular in biological work, both in vivo and in vitro. We have previously shown these CNPs have some potential to treat wound care, cancer therapy, retinal protection and neurodegenerative diseases. However there are several factors to consider, one being its interaction with biological molecules in different buffers, media, and serum. The common anions are phosphate, sulfate and carbonate. In our previous work, CNPs interaction with sulfate and carbonate are proven not to alter the surface chemistry of CNPs, whereas phosphate anions do. The CNPs properties are surface dependent and phosphate anions are shown to modify the surface. Current study focuses on preventing the CNPs surface modification by phosphate buffer through functionalization. Dextran and polyethylene glycol (PEG) were used to functionalize CNPs. The functionalized CNPs were incubated with phosphate ions and changing their absorbance and emission characteristic was analyzed by Ultraviolet-visible spectroscopy (UV) and photoluminescence spectroscopy (PL). The results show that CNPs functionalized with Dextran prevented interaction with PBS (phosphate ions) and preserved the redox property of the nanoparticle. However, PEG coating fails to do so. Varying pH levels in the range of 6-8 had no significant effect on the phosphate ion interaction with CNPs surface. We further investigated the surface interaction of PEG-CNPs with phosphate, while varying the concentration (5% to 40%) and the chain length (300 molecular weight to 6000 molecular weight) of PEG. The results showed that increasing the concentration or chain length of PEG did not have any effect on phosphate and cerium surface interaction. Looking into the surface charge and morphology of PEG and Dextran will allow us to gain further insight into what is occurring on the surface of these nanoparticles with phosphate ions. This basic study will help to engineer CNPs, which will be effective in biological applications and overall to prevent modification of CNPs surface.

BI-TuP4 Surface Topographic Patterns Functionalized with Different Biomaterials for Studying Neural Cell Behaviors, ***Y.P. Lu***, *M.Y. Lin*, National Applied Research Laboratories, Taiwan, Republic of China

Micro- and Nano-patterned substrates functionalized with extracellular matrix (ECM) have been recognized as powerful tools for regulating cell behaviors and functions, because biomimetic features enable the study of cellular responses to specific external stimulations. Surface topography in micro- or nano-scale contributes to provide a physical niche to resemble the physiological environment, whereas biomolecules in ECM can provide a cell-favorable environment in the artificial materials. Independent combination of topographical fabricated scaffolds and biomaterials with bioactive features have provided a suitable *in vitro* cellular function study system. We developed two different characteristics of polymer chips with microstructure and functionalized peptide, including polydimethylsiloxane (PDMS) chip modified with poly-D-lysine (PDL) peptide on the surface and silicon wafer modified with laminin-1 peptide on the surface. The PDMS chip was composed of ridges and grooves around 10 μm in width to form a stripe pattern with micro-meter scale. Another silicon substrate was prepared from micro-meter stripe pattern with nanorods in the grooves region. Neuron-like PC12 cells were then cultured on these 3D substrates and stimulated to manifest different behaviors, and induced cell differentiation with nerve growth factor (NGF) treatment. PC12 cells were cultured in biomimetic substrates impacted in several properties: Cells displayed contact guidance on both substrates and became elongated along the grating axis of scaffolds. When neuron cells cultured on the PDMS substrate, soma and neurite grew on the ridge, groove, or even lateral wall and formed the overlappin g distribution. On the other hand, PC12 cells grew on the nanorod substrate functionalized with laminin and displayed contact guidance and became parallel elongated along the flat ridge plane. Some neurites were able to cross groove through the nanorod-supported laminin bridge. Results gained from this study provide the manipulation of neuron cell fate by using enhanced patterning techniques and would be

valuable in various biomedical applications, including tissue engineering, neuron regeneration, and basic cell biology.

BI-TuP5 Nanoscale Characterization of Acid and Thermally Treated Collagen Fibrils and its Effects on the Cellular Responses of Osteoblast, ***Y.J. Park***, KAIST, Republic of Korea, *G.J. Choi, S.H. Kim, J.H. Hahn, T.G. Lee,* KRISS, Republic of Korea, *W.J. Lee,* KAIST, Republic of Korea, *D.W. Moon*, KRISS, Republic of Korea

Type I collagen is a major extracellular matrix component and its hierarchical structure plays an important role in the regulation of cellular behavior. In order to study the effect of structure, surface chemistry, and mechanical properties change of collagen fibril on the cellular response, various collagen structures were prepared by different degrees of acidic and thermal treatment of native collagen fibrils. First, to study the microstructure and morphology of collagen, atomic force microscopy (AFM) was used due to its high spatial resolution and surface morphology specificity. Second, we applied time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the surface chemistry changes of collagen fibrils by utilizing the capability of providing molecular surface chemical information. Third, to observe the changes in the mechanical properties during acidic and thermal treatment of collagen fibrils, contact-resonance force microscopy (CR-FM) was applied because of its ability to provide not only nanoscale spatial resolution but also quantitative information about the mechanical properties. It was demonstrated that the change of microstructure, surface chemistry, and mechanical property of collagen induced by acidic and thermal treatment could be observed in molecular level using AFM, ToF-SIMS, and CR-FM. The structural, chemical, and mechanical properties of acid and thermally treated collagen fibrils could be correlated with the cellular responses such as cell morphology, cytoskeleton organization, and viability.

BI-TuP6 Comparison between Fabrication Techniques for Glass Microfluidic Microchannels, ***C. Vélez***, *S. Silva,* Universidad de los Andes, Colombia, *X. Wang,* University of Florida, *A. Gonzalez-Mancera, C. Leidy, J.F. Osma,* Universidad de los Andes, Colombia, *F. Ren*, University of Florida

This work presents a comparison between three microfluidic fabrication techniques for shallow channels (less than 20µm depth) on glass including laser scribing, wet chemical etching using photoresist as a mask, and wet chemical etching using copper deposition as a mask. The purpose of this device is to perform optical particle tracking using a Four Roll Mill configuration. A JPSA excimer UV laser system was used to perform the laser scribing process. This process proves to be the fastest, allows for better control over the etching rate, and produces smallest angles at the edges. On the other hand, wet etching with copper as a mask uses hydrofluoric acid to produce the channels, and the process proves to be better than etching with photoresist mask. Wet etching with copper as mask also shows better transparency at the bottom of the microchannels, which is perfect for optical tracking and a more homogeneous etching than laser scribing; however, it uses more time and there is less control over the etching rate. Complex geometrical patterns as semicircles and intersections were better obtained using wet etching with copper than the other two fabrication techniques. Liquid flowing inside complex geometry patterns was simulated with Comsol Multiphysics V 4.2. Final fabricated devices were tested with two micro-particle solutions: alginate particles and lipid vesicles in aqueous solutions.

BI-TuP7 Ceria-Gold-Chitosan Nanosystem with Improved Redox Activity and Enhanced Imaging, ***S. Barkam***, *S. Das,* University of Central Florida, *P. Kulkarni, S. Mallik,* North Dakota State University, *S.S. Seal*, University of Central Florida

Research advances in nanoparticles constructs intended for biomedical applications have proved to be of major importance. This often presents serious challenges in terms of imaging or tracking of the nanoparticles. Our research aims at developing a system that has the effective characteristics of therapeutics and imaging modality. It is well known that Reactive oxygen species (ROS) and nitrogen species play a critical role in many oxidative stress associated disorders like cancer, neurodegeneration, radiation induced tissue damage. Ceria nanoparticles (CNPs) have proved to be potential redox active radical scavenging agents which also exhibit superoxide dismutase and catalase mimetic activity. These nanoparticles can potentially act as antioxidant which is attributed to its redox nature of switching the oxidation states from +3 to +4 mediated at the oxygen vacancies on the surface. Recent research has shown progress in the study of enhancing the contrast in imaging using gold nanoparticles by various microscopy techniques such as TEM, Computed tomography (CT) etc. Its marker ability is attributed to the strong plasmon enhanced absorption and increased light scattering ability which gives detailed information of the location of gold particles by combining optical and electronic microscopy. It is also proven to be non toxic and biocompatible *in vivo*. Our research attempts on providing a formulated coupling of the above notions to form a CNP-Chitosan-Gold integrated system. Addition of Chitosan helps in the reduction of $HAuCl_4$ to form gold nanoparticles and this polymer also enables the biocompatibility of the imaging agent. The activity of CNPs can be improved by surface modification through selective functionalization thereby enhancing the redox behavior and stability of the system.

BI-TuP8 The Effect of Light-Induced Surface Modification of Functionalized Ceria Nanoparticles towards Killing of Skin-Derived Cancer Cells, *S. Barkam, S. Das, V.P. Perez,* ***S.S. Seal***, University of Central Florida

Malignant melanoma is the sixth most common cancer diagnosed in the United States. Surgery, chemotherapy and radiation are some of the successful techniques in killing tumor cells. However, in these techniques, it is not easy to distinguish tumor cells from the healthy once which inadvertently get exposed to chemical agent/radiation. Therefore it is required to develop an anti-cancer agent which selectively kills the cancer cells, while still protecting the normal tissues. In our preliminary work, we have shown that Dextran (1000Da) coated Cerium oxide nanoparticles (Dex-CNPs) selectively kills the cancer cells (50% killing at a concentration of 150µM) without inducing toxicity to normal cells. However, the mechanism involved on how CNPs/Dex-CNPs attain the selectivity and efficiently kill the tumor cells is still unknown. In this study we have synthesized Dextran coated ceria nano particles (Dex- CNPs) with different surface oxidation state ratio (Ce^{4+}/Ce^{3+}) but similar shape and size. This will provide an in depth understanding of the key chemical and physical properties of the system that can improve its efficacy. The varied surface oxidation of the particles is achieved by exposing Dex-CNPs to light which initiates a color change from dark to pale yellow indicating the reduction of Ce^{4+} to Ce^{3+}. Interestingly we have found that the Dex-CNPs exposed to light have reduced cytotoxicity towards squamous cell carcinoma cell line (CCL30) compared to the protected once. Characterization of the same revealed that Dex- CNPs exposed to light have decreased Ce^{4+}/Ce^{3+} surface oxidation ratio compared to the other. This provides more insight in useful synthesis of Dex-CNPs in terms of storage and handling. In summary, higher Ce^{4+}/Ce^{3+} surface oxidation ratio is more efficient in hindering tumor growth by effectively hindering the tumor-stoma interaction.

BI-TuP9 Stability and Dispersion Characterstics of Ceria Nanoparticles in Biological Media, ***P. Munusamy***, *T. Suntharampillai, D.R. Baer*, Pacific Northwest National Laboratory

Although nanoparticles have wide variety of biomedical applications, the characteristics that produce beneficial or toxic effects are not well understood. Some ceria nanoparticles have gained high visibility for their redox active properties which appear to serve as free radical scavengers. Toxicity measurements of various types and sizes of ceria nanoparticles tested with a variety of *in-vitro* and *in-vivo* studies have many apparent inconsistencies. To accurately evaluate *in-vitro* and *in-vivo* testing results it is important to understanding the properties and behaviors of the ceria particles in the media in which the tests are conducted. In this work, ceria nanoparticles prepared by thermal hydrolysis process are used as a model nanoparticle to study there stability and dispersion characteristics. The particles behaviors in biological media such as aggregation and sedimentation rates were systematically evaluated by aggregation kinetic analysis and sedimentation studies. As one example, fetal bovine serum (FBS) which consists of multiple proteins components was found to be an effective dispersion agent forming a relatively robust surface layer with 24 hours. Data on mixtures of common biological media solutions show a variety of differing impacts. The type of kinetic data we have collected provides important information regarding behavior of nanoparticles in different dispersion media which valuable in understanding toxicity and other biological impact studies.

BI-TuP10 An Anti-biofilm Formation Design Strategy Based on Fibrous Topographical Cues, ***M. Kargar***, *A.S. Nain, B. Behkam*, Virginia Tech

Biofilms tend to be significantly less responsive to antimicrobial stressors, compared with planktonic bacteria. Studies on the natural antifouling surfaces have shown that most of them have well organized micro/nanoscale surfaces features. This work aims at improving the current understanding of the effects of well-defined sub-micron surface topographies on microorganism-surface interactions with the ultimate goal of developing a bioinspired antifouling design framework based on topographical cues. To this end, model surfaces with well-defined surface topographies in form of highly aligned polystyrene nano fibers at controlled separation distances (diameter (D_f). 90 nm-900 nm and Separation distance (S_f): 0 nm-5000 nm) were fabricated using our previously developed pseudo-dry spinning method. *Pseudomonas aeruginosa* strain PAO1 (diameter (D_b)≈ 500nm, length (L_b)≈ 1800nm) was then presented on the nanofibrous surfaces in a 2.5-hour static retention assay. Scanning electron

microscopy was utilized to quantify linear attachment density (number of bacteria/fiber length) and the degree of alignment between bacteria and fibers for all combination of fiber diameters ($D_f < D_b$,$D_f \approx D_b$, $D_f > D_b$) and spacing ($S_f < D_b$,$S_f \approx D_b$, $D_b < S_f < L_b$, $S_f > L_b$) at single cell level. Our experimental results demonstrate the presence of an optimum antifouling geometrical condition related to the minimum experimental adhesion density. This optimum condition occurs when the fiber diameter is close to the bacteria diameter ($D_f \approx D_b$) and the spacing is less than the bacteria diameter ($S_f < D_b$)). Comparing to the bare surface this geometrical combination reduces bacterial adhesion by more than 40%. Additionally, the SEM images show that bacteria developed microcolonies (onset of biofilm formation) on the bare samples while the engineered surface inhibited colony formation. Our data reveal strong similarity between thermodynamic underpinnings of bacteria – surface interactions and vesicle– surface interactions. The thermodynamic principles governing the vesicle-rigid surface interactions were used to interpret the experimental data and explain the experimentally observed optimum antifouling topographical condition using an energy-based approach. Furthermore, a systematic design methodology for empirical determination of the optimum antifouling topographical condition for nanofiber textured surfaces is outlined.

BI-TuP11 Synthesis of Redox Active Cerium Oxide Nanoparticle with Varying Size and Shape by Manipulating the Chain Length of PEG, ***S. Das****, C. Neal, A. Kumar,* University of Central Florida*, A.S. Karakoti,* Pacific Northwest National Laboratory*, S.S. Seal*, University of Central Florida

The objective of this study is to ascertain the role of different molecular weights polyethylene glycol (PEG) solvents on the redox property of cerium nanoparticles. PEG with molecular weight of 300, 600, 1500, 3400 and 6000 were selected in this study for preparing 5mM cerium oxide nanoparticles (CNPs) in 20% PEG medium. The size and morphology of the particles were analyzed using TEM. Interestingly, the size and shapes of the nanoparticles were observed different in different chain length of the PEG nanoparticles from round to star shaped. The red-ox state of the samples was accessed at regular intervals, until stability was observed, using UV-Vis spectroscopy. Absorbance of each sample was recorded in the range of 250nm to 600nm. All the PEG-CNPs sample revealed stable peak at 298nm (characterstic of Ce^{3+}) with additional minor peak observed at 380nm for 1500, 3400 and 6000 PEG-CNPs sample. The biological activity measured by superoxide dismutase mimetic assay was found to be similar for all the PEG-CNPs. The current research suggests that by changing the chain length of the PEG it is possible to synthesize different size and shape of the PEG-CNPs with similar redox activity for specific applications.

BI-TuP12 In Vitro Protein-Biofilm on Nanoparticles Characterizated by ToF-SIMS, STEM and TEM, ***H.P. Wiesmann****, J. Neunzehn,* Technische Universität Dresden, Germany*, F. Draude, H.F. Arlinghaus*, University of Muenster, Germany

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was applied to detect and characterize different nano scaled protein coatings on gold nanoparticles. After washing the nanoparticles by various steps, the gold particles (diameter of about 10 to 20 nm) were coated with the proteins collagen type I and fibronectin and also different protein combinations in thin mono layers. The different nano-scaled protein layers on the cleaned gold nanoparticle surfaces were identified by detection of the protein typical amino acid mass peaks by time-of-flight secondary ion mass spectrometry.

In addition, the protein-coated particles were investigated by transmission electron microscopy to get information about the proteins structure and their layer thickness on the particle surfaces. It was possible to distinguish the protein coatings by their molecule thicknesses and to evaluate the different particle agglomeration influenced by the used proteins by the use of scanning transmission electron microscopy.

BI-TuP13 A Novel Method for the Bio-conjugation of Catalytic Nanoparticles, ***R. Draper****, S. Das, S.S. Seal***, University of Central Florida

This paper explores the possibility of using bio-conjugation to disperse nanoparticles into composite matrices for catalytic purposes. Solid state catalysis is a complex mechanism which can be drastically affected by catalyst size, morphology, surface condition, concentration, dispersal, and location to critical reaction sites. To better understand these mechanisms, as well as to tune solid catalysts to have the greatest specific effect, it is sometimes desired to arrange them into difficult to achieve, high free energy formulations. To overcome their natural characteristics, templating bio molecules can be used to arrange the particles into these difficult formulations to more completely understand the kinetics of the catalysis. One of the more prevalent methods of nanoparticle conjugation involves Watson-Crick base pairing, a method not suitable for aggressive solvents, or for conjugating many types of particles. Here we explore a novel method for biomolecule based nanoparticle conjugation with application to dispersion of catalytic particles in a solid matrix. The effects of these various dispersions are then studied using microscopic, spectroscopic, and colorimetric methods.

BI-TuP14 A Microfluidic Study of the Interaction of Haematopoietic Stem Cells with their Microenvironment, ***M. Hanke****, C. Christophis, C. Leinweber,* Institute for Functional Interphases, KIT, Karlsruhe, Germany*, N. Baran, I. Taubert, P. Wuchter, A. Ho,* University Hospital Heidelberg, Inner Medicine V, Germany*, A. Rosenhahn*, Institute for Functional Interphases, KIT, Karlsruhe, Germany

A microfluidic adhesion assay has been developed to quantitatively investigate the interaction of cells with interfaces under well defined flow conditions.[1] The device was applied to the study of the interaction of leukaemic cells and haematopoietic stem cells with hyaluronic acid surfaces. We found that beyond a critical shear stress the cell surface receptor CD44 mediates a catch bond, flow induced rolling of the cells on the surfaces[2], similar as observed for leukocytes during the extravasation process.[3] A similar rolling phenomenon occurred on mesenchymal stroma cells, which are present in the bone marrow niche creating the microenvironment required for haematopoietic stem cells to endlessly proliferate. The mesenchymal stroma cells inter alia secrete the stroma-cell-derived factor-1 alpha which has been reported to activate stem cell migration, mobilization and homing.[4] The effect of this chemokine on the movement of haematopoietic stem cells was also studied utilising a novel microstructured niche model.

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[4] Jing DH, Fonseca AV, Alakel N, et al. Haematol-Hematol J. 2010, 95, 542-550.

BI-TuP16 Nonfouling Amphiphilic Polysaccharides, ***S. Bauer****, M.P. Arpa-Sancet,* Ruprecht-Karls University Heidelberg, Germany*, J. Finlay,* University of Birmingham UK*, N. Aldred,* Newcastle University, UK*, M.E. Callow, J.A. Callow,* University of Birmingham UK*, A.S. Clare,* Newcastle University, UK*, A. Rosenhahn*, Karlsruhe Institute of Technology, Germany

The potential of polysaccharides for fouling-resistant coatings lies in their chemical structure: due to the presence of ether- and hydroxyl-groups, they are highly hydropihilic and able to form water-storing hydrogels. In this study, the free carboxyl-groups of two surface-tethered polysaccharides, hyaluronic acid (HA) and chondroitin sulfate (CS) were postmodified with the hydrophobic trifluoroethylamine. This strategy was chosen to study different effects: a blocking of free carboxyl groups to prevent complexation of bivalent ions and to preserve the resistance of these coatings in the marine environment, a shifting of the contact angle towards the minimum in the Baier curve and the introduction of amphiphilic properties due to the hydrophobic fluoro-groups. The coatings were tested towards their protein resistance and with different fouling relevant species to evaluate their resistance properties. Settlement and adhesion strength of the marine bacteria *Cobetia marina* and the two algae species *Ulva linza* and *Navicula perminuta* were reduced by the modification in case of HA based coatings. However, in case of CS coatings, the adverse effect was observed.

BI-TuP18 STM Characterization of Chemically Prepared Peptide-Functionalized Monolayers, ***A. Raigoza****, L. Webb***, The University of Texas at Austin

Proteins are able to express catalytic and sensing functions that current technologies are unable to reproduce. Instead, efforts have been focused on properly integrating this functionality with non-biological materials. Unfortunately, proteins are generally observed to lose function because of unfolding, aggregation, and overall loss of structure that occurs when a soft, solution-phase material is placed in the harsh structural and electrostatic environment that occurs on and near surfaces. To improve protein-surface interactions, we create a surface that is composed of peptides, which can be tailored for specific protein attachment. Here, we present scanning tunneling microscopy (STM) images of peptide-terminated monolayers on a gold surface created by functionalizing alkanethiol self-assembled monolayers. A Huisgen cycloaddition "click" reaction is used to tether the peptides to the surface at reactive locations that line up with modified residues on the peptide. STM is used to image the surface at each reaction step with molecular resolution. A complete surface reaction would generate a peptide density of approximately 0.6 peptides/nm^2, based on the distance between reactive azide functional groups and the theoretical size of our

peptide. We estimate 0.4 peptides/nm^2 based on the area covered by peptides in our images.

Biomaterial Interfaces
Room: 23 - Session BI+SS+NS-WeM

Bio/Nano Interfaces with Applications in Biomedicine and Energy

Moderator: G.J. Leggett, University of Sheffield, UK

8:00am **BI+SS+NS-WeM1 Combining Colloidal Lithography and Photolithography to Create Dual Length-Scale Topographical Features to Study Stem Cell Behavior**, ***D.T. Bennetsen***, *D.C.E. Kraft, R. Ogaki, M. Foss*, Aarhus University, Denmark

It is well known that topographical features influence cellular response. A novel combination of colloidal- and photolithography has been developed to create a dual length scale topographical platform. The presented approach permits rapid parallel fabrication of micro/nanoscale patterns. The aim is to study the response of primary human dental pulp stem cells (hDPSC) to such topographies in a systematic way.

Colloidal lithography is performed using the "lift-off" method, which is applicable to surfaces with a non-flat surface. This enables the combination of using photolithography pre-made wafers as substrates, resulting in a complex topographical structure, spanning two length scales (Figure 1). Topographical patterns are created using the colloidal mask with either evaporation or sputtering via physical vapor deposition (PVD). The principle combination of materials investigated is tantalum covered with tantalum features. These dual scale substrates are exposed to hDPSC and proliferation, attachment and differentiation are examined. Differentiation is examined using osteogenic markers and MyoD1 expression.

Initial cell proliferation data indicates that variations in the colloidal pattern heights do not seem to elicit a statistical significant response (Figure 2). A set of experiments to clarify the effect of the colloidal pattern on the proliferation and cell cycle of the hDPSC is thus currently being performed. Furthermore, the effect of the dual scale topographical substrates on proliferation, differentiation and cell cycle is also being explored.

Concurrently we are investigating the combined effects of topographical/chemical patterns on cellular response. This can be achieved by depositing different materials site-specifically, followed by a material-specific self-assembly route. E.g. silanes and thiols with specific chemical moieties on oxides and gold, respectively. Characterization is performed using atomic force microscopy (AFM), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Our fabrication approach enables the opportunity to increase the complexity of artificial 2D platforms thus by gaining a better understanding of cellular behavior for a range of biomedical and biotechnological applications.

8:20am **BI+SS+NS-WeM2 Genetically Modified *Tobacco Mosaic Virus* (TMV)-based Electrochemical Detection of 2, 4, 6-trinitrotoluene (TNT)**, ***F. Zang***, *H. Ben-Yoav, X. Fan, A. Brown, J. Culver, R. Ghodssi*, University of Maryland

Detection of chemical hazards and explosive compounds has received growing attention for applications in environmental monitoring, food science, and national security. Explosives, such as TNT, show low vapor pressure, molecular mass, and volume, which makes the detection of these molecules challenging for most mass and refractive index based sensors. Thanks to the redox reaction of nitro groups in TNT molecules, electrochemical methods may be used for detection of low concentrations of TNT in aqueous environments. Electrochemical sensors are suited for on-site explosive detection due to high sensitivity, low volume and convenient integration with miniaturized devices. However, to distinguish TNT from other electrochemically active compounds in complex environments, high selectivity is a more critical factor for development of TNT sensors.

The TMV has a high aspect ratio, rod-like nanostructure that can be genetically modified to express tailored chemical receptors. In this work, a 12-amino acid (WHWQRPLMPVSI) sequence peptide with multivalent recognition properties of TNT was expressed on the coat protein of TMV (TMV-p) which was utilized to develop a sensitive and selective electrochemical sensing mechanism for TNT detection. Selective binding of TMV-p with TNT molecules will decrease the free TNT concentration in solution, reducing the number of nitro groups available for redox reactions.

In preliminary studies, background signals generated from electrolytes were characterized and the signal-to-noise ratio was optimized by long term scans of square wave voltammetry. Three concentration dependent current peaks from the reduction of nitro groups in TNT were observed at the potentials of -0.53V, -0.72V and -0.86V vs. Ag/AgCl reference electrode, respectively, which agreed with the results in literatures. The initial results showed a stable and reliable electrochemical response by the TMV-p sensing system. By comparing the reduction currents in the mixtures of TMV-p and unmodified TMV with TNT solutions, we will demonstrate that TMV-p preserves the peptide binding affinity to TNT molecules while increasing the binding site density.

The approach described in this study is a sensitive and selective label-free method to detect TNT based on the binding of target molecules with peptide modified TMV. In addition to the highly selective peptide binding with analytes and a high binding site density, the genetically modified TMV is also capable of self-assembly, coating the active surfaces of a wide range of transducers. This work can potentially be implemented in the development of miniature sensors for selective TNT detection in complex environments.

8:40am **BI+SS+NS-WeM3 Nanoparticles in Biology: Engineering the Interface for Sensing and Delivery**, ***V. Rotello***, University of Massachusetts **INVITED**

A key issue in the use of nanomaterials is controlling how they interact with themselves and with the outer world. Our research program focuses on the tailoring of nanoparticles of surfaces for a variety of applications, coupling the atomic-level control provided by organic synthesis with the fundamental principles of supramolecular chemistry. Using these engineered nanoparticles, we are developing particles for biological applications, in particular delivery and sensing. This talk will focus on the interfacing of nanoparticles with biosystems, and will discuss our use of nanoparticles for delivery applications including our *in vitro* studies of small molecule, nucleic acid, and protein delivery. This presentation will also feature the use of nanoparticles for diagnostic applications, including the use of array-based sensing paradigms for the sensing and identification of proteins, bacteria and cell type and state.

9:20am **BI+SS+NS-WeM5 Hydrophobic Forces, Electrostatic Steering, and Acid–Base Bridging between Atomically Smooth Self-Assembled Monolayers and End-Functionalized PEGolated Lipid Bilayers**, ***M. Valtiner***, Max-Planck-Institut fur Eisenforschung, Germany, *S.H. Donaldson, M.A. Gebbie, J.N. Israelachvili*, University of California, Santa Barbara

A molecular-level understanding of interaction forces and dynamics between *asymmetric* apposing surfaces plays a key-role in utilizing molecular structures for functional surfaces in biological and materials applications. To quantify interaction forces and binding dynamics between apposing surfaces in terms of their molecular architecture we developed a novel surface-forces-apparatus experiment, using self-assembled monolayers (SAMs) on *atomically-smooth* gold. Varying the SAM head-group allowed to quantitatively identify and control which interaction forces dominated between the SAM surfaces and surfaces coated with short-chain, end-functionalized polyethylene-glycol (PEG) polymers extending from lipid-bilayers [1].

Three different SAM-terminations were studied: (a) carboxylic-acid, (b) alcohol, and (c) methyl head-group terminations. These functionalities allowed for the quantification of (a) specific acid-base bindings, (b) steric effects of PEG chains, and (c) adhesion of hydrophobic segments of the polymer-backbone, all as function of the solution pH. The pH-dependent acid-base binding appears to be a *specific, charge-mediated hydrogen bond* between oppositely-charged carboxylic-acid and amine functionalities, above the acid-pK_A and below the amine-pK_A. The long-range electrostatic "steering" of acid-base pairs leads to high binding probability even at distances close-to-full-extension of the PEG tethers, a result which has potentially important implications for protein-folding, enzymatic catalysis and biomaterial development.

[1] M. Valtiner et al., *JACS*, **2012**, 1746

9:40am **BI+SS+NS-WeM6 Viral Encapsulation in Lecithin Liposomes to Enhance the Therapeutic Effect of Oncolytic Viral Therapy**, ***N. Mendez***, *V. Herrera, A.C. Kummel*, University of California San Diego

Oncolytic viruses have emerged as a novel platform for cancer therapeutics due to their tumor-selective replication in cancer cells. 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. Extensive testing of oncolytic viruses has shown a limited therapeutic effect due to rapid clearance by the reticuloendothelial (RE) system and antibody neutralization. With the aim to overcome an immune response and to enhance localized delivery, an oncolytic virus-liposomal encapsulation method has been designed to increase tumor uptake and the therapeutic efficacy of oncolytic viruses in

cancer cells. An inexpensive, non-toxic liposome has been prepared by self-assembly of Lecithin phospholipid bilayers around the Adenovirus capsid. Cholesterol and DSPE-PEG were incorporated into the lipid formulation to improve retention and stability. The developed method has shown that non-targeted encapsulated viral particles retain their ability to transfect cancer cells. In addition, surface functionalization of the liposomes may be applied to specifically target cancer cells and to compensate for decreased infectivity due to viral encapsulation.

10:40am **BI+SS+NS-WeM9 Engineering Bio-Interfaces using Electric Field-Induced Nanolithography**, ***S. Zauscher***, *R.J. Ferris, B. Yellen*, Duke University

Field-Induced Nanolithography (FINL) offers a convenient tool to create physically or chemically distinct patterns for bio-interfacial sensing applications. For pattern transfer, FINL merely requires a conductively coated SPM tip or stamp, connected to a conductive substrate via a voltage source. The patterning electrode is placed in contact with the target surface and a bias voltage is applied. Few sub-diffraction limit surface patterning techniques offer FINL's versatility to function in both a serial and parallel fashion. Recently we demonstrated the use of FINL to pattern a range of polymer brushes: poly(acrylic acid) (PAA), poly(N-isopropylacrylamide) (PNIPAAm), poly(sulfobetaine methacrylate) (PSBMA), and poly(oligo(ethylene glycol) methyl methacrylate) (POEGMA). Our results show that FINL of non-fouling polymer brushes provides a novel patterning technique that results in the localized topographical and chemical modification of the polymer brush surface only. The resulting chemical modification allowed selective addressing of the brush surface with aldehyde reactive coupling chemistries. Our approach thus shows significant promise for fabricating large-scale sensing devices, as patterning can be accomplished in a step-and-repeat fashion. Using FINL, we also demonstrated patterning of surface charges onto ferroelectric thin films (FETFs). FETFs are materials that are able to maintain a bi-stable polarization state, and that once polarized, maintain a high surface charge density. Using FINL, it is possible to locally align unit-cell dipole moments within the film to produce nano-scale polarization patterns. Although to date the use of FETFs is isolated to semiconductor and memory applications, we demonstrate that FETFs have great potential for biological and interfacial sensing applications. We show that FETF surface charge patterns can be used to control the lateral extent of electric double layer formation in dilute electrolyte solutions, with clear implications for field assisted particle deposition and programmed self assembly.

11:00am **BI+SS+NS-WeM10 Supramolecular Bioassemblies at Solid-Liquid Interfaces: Binding Control through Redox-Driven Multivalent Host-Guest Interactions**, ***G.V. Dubacheva***, CIC biomaGUNE, Spain, *L. Guerente, D. Boturyn,* Joseph Fourier University, France, *R. Auzély,* CERMAV, France, *R.P. Richter,* CIC biomaGUNE, Spain; Joseph Fourier University, France; Max Planck Institute for Intelligent Systems, Germany, *P. Labbé*, Joseph Fourier University, France

The design of kinetically stable bioassemblies while keeping binding control is of high current interest for bioanalytical and biomedical sciences. The development of tunable biointerfaces is also a key issue in nanobiotechnology as they can be used for modeling cell surface-associated biological processes. In this context, supramolecular host-guest chemistry is particularly attractive as it allows controllable molecular recognition and structural modification at specific areas of a nanoassembly, i.e. purpose-designed molecules can be confined in time and space in a highly controlled manner.

Cyclodextrin (CD) is well-known to form host-guest complexes with hydrophobic molecules while being soluble at physiological conditions. Taking advantage of redox-driven β-CD-ferrocene (Fc) multivalent interactions, we designed stimuli-responsive biomaterials composed of linear polymers, their multilayer assemblies and biomolecules. For this aim, we developed a new method to create β-CD self-assembled monolayers (SAMs) allowing precise varying β-CD surface density.1 We showed that Fc-functionalized polymers can be reversibly attached to such β-CD SAMs.1 We also showed a possibility to build up multilayer host-guest polymer assemblies on β-CD surfaces.2 In addition, we applied these β-CD SAMs for the reversible attachment of biomolecules using orthogonal Fc/β-CD- and specific bio-interactions under biological conditions.3 Finally, combined with guest-modified polysaccharide hyaluronan, the β-CD surfaces were explored as a model system to understand multivalent interactions at the cell-hyaluronan matrix interface associated to a variety of cellular functions and biological processes.

Physico-chemical properties of supramolecular assemblies were characterized by QCM-D, ellipsometry, cyclic voltammetry and contact angle goniometry. The redox-driven binding of polymers and biomolecules to β-CD surfaces was assessed by *in situ* combining electrochemistry/QCM-D and SPR ellipsometry/microfluidic systems. The developed tunable biointerfaces can be applied to investigate other topics in soft condensed matter physics, molecular physics and biophysics.

1Dubacheva et al., *Langmuir*, **2010**, 26:13976

2Dubacheva et al., *Soft Matter*, **2010**, 6:3747

3Dubacheva et al., *Chem Commun*, **2011**, 47:3565

11:20am **BI+SS+NS-WeM11 High-resolution *In Situ* Electrochemical STM Imaging of Phospholipid Model Cell Membrane**, ***H. Shimizu***, *S. Matsunaga,* University of Tokyo, Japan, *T. Yamada, T. Kobayashi,* RIKEN, Japan, *M. Kawai*, University of Tokyo, Japan

We obtained molecular-scale images of phospholipid layers spread on a modified Au(111) immersed in a buffer solution, by means of *in situ* electrochemical scanning tunneling microscopy (EC-STM). Real cell membranes consist of a bilayer of phospholipids which continually gather and interact. There are various kinds of phospholipids in the real cell membranes. To understand the action of these molecules, a dynamic molecular-scale method of observation is necessary. Lipkowski [1] first visualized static monolayers of phospholipid on Au(111) by *in situ* EC-STM. Matsunaga *et al.* [2] revealed dynamic, microscopic motion of phospholipid monolayer on alkanethiol-modified Au(111) immersed in a buffer solution. We intended to compose a bilayer of phospholipid on a hydrophilic substrate in order to mimic the real cell membrane more truly. We used a hydrophilically modified Au(111), anticipating that the first lipid monolayer with the hydrophilic head group down to the surface, and the second lipid monolayer with the hydrophobic alkyl chains down, all spontaneously in aqueous buffer solution.

For this purpose, we used 3-mercaptopropionic acid (MPA) self-assembled monolayer (SAM) on Au(111), in which the COOH groups are expected to be exposed out of the surface. We first observed a ($\sqrt{3}$ x $\sqrt{3}$) type adlattice of MPA SAM by STM. Then the sample was immersed in 50 mM phosphate buffer containing minimal lipid particles of 200 μM 1-palmitoyl-2-oleoyl-*sn*-glycero-3-phosphocholine (POPC) with or without 50 μM cholesterol.

We uniquely observed a 2-dimensional adlattice with a parallelogram unit cell of 1.0 nm x 1.9 nm. Along the short segment, blight spots are aligned. The adlattice did not change with or without cholesterol, indicating that it was composed exclusively of pure POPC. The interval of 1.9 nm is apparently shorter than the full length of POPC molecule (≈2.5 nm). To interpret the adlattice structure, we considered a model structure composed of tilted POPC, with the head group attached to the MPA SAM. This model involves a strong affinity between the hydrophilic groups.

Although this frozen adlattice does not completely match our target structure of mobile lipid bilayer, we consider we could partly utilize the hydrophobicity/hydrophilicity of the phospholipid molecules to compose a uni-directional membrane. We will further develop this kind of methods by choosing the proper modifier on Au(111), aiming the bilayer structure. By this we expect to go closer to the nanometer-scale reality of cell membranes containing functional proteins.

[1] J. Lipkowski, *Phys. Chem. Chem. Phys.* **12**, 13874 (2010).

[2] S. Matsunaga *et al.*, *Electrochem. Commun.* **9**, 645 (2007).

11:40am **BI+SS+NS-WeM12 Characterization of Polymer/Drug Films as Model for Drug Eluting Coronary Stent Coating Layers**, ***V. Ciarnelli***, *M.R. Alexander, M.C. Davies, C.J. Roberts*, University of Nottingham, UK

This work describes the characterization of a polymeric based drug eluting stent coating, used in coronary stenting to prevent restenosis [1]. The work examines thin films as models for drug eluting stent coatings. Complementary surface analysis techniques are used to investigate the drug polymer distribution on the surface and throughout the depth of the model films.

The first goal of this project is to establish the feasibility of certain surface analysis techniques in the characterisation of a drug eluting stent coating layer. Secondly, this study will act as a standard reference to determine the ideal operating conditions for characterizing the more complex stent device.

Thin film models were produced varying the substrate materials (silicon or glass), preparation procedures (spin casting or spray coating) and drying methods (oven or warm air). The different drug to polymer ratios used were: 1:3, 1:1 and 3:1 (w:w).

Complementary surface analysis techniques such as atomic force microscopy (AFM), time of flight secondary ion mass spectrometry (ToF-SIMS) and x-ray photoelectron spectroscopy (XPS) were employed for the characterization of the films. Depth profiling has also been performed using XPS and ToF-SIMS.

AFM imaging of the oven dried spun cast films shows domains of drug, characterized by a circular organization with features of 100 - 250 nm in

diameter. These domains are not observed in other samples and appear to be related to phase separation during the drying step.

Surface characterization using XPS shows enrichment of the drug at the surface for all the model films with the exception of the spray coated films at the 1:3 drug-to-polymer weight ratio.

Depth profiling using both ToF-SIMS and XPS confirms that the drug is enriched at the surface, posing significant implications for drug loaded polymer delivery systems.

Complementary surface analysis techniques have proven extremely successful in characterizing the model films. Suitable techniques and their operative conditions have now been established for the characterization of a stent device.

[1] I. Iakovou et al., Incidence, predictors, and outcome of thrombosis after successful implantation of drug-eluting stents. JAMA,. **293** (2005): p. 2126-2130.

Graphene and Related Materials Focus Topic
Room: 13 - Session GR+AS+BI+PS+SS-WeM

Graphene Surface Chemistry, Functionalization, Biological and Sensor Applications
Moderator: D.K. Gaskill, U.S. Naval Research Laboratory

8:00am **GR+AS+BI+PS+SS-WeM1 Structural Analysis of Chemically Functionalized Epitaxial Graphene with High-Resolution X-ray Reflectivity**, *J.D. Emery, Q.H. Wang, M. Zarrouati,* Northwestern University*, P. Fenter,* Argonne National Laboratory*, M.C. Hersam,* ***M.J. Bedzyk***, Northwestern University

For graphene to realize its potential in next-generation electronics it must be incorporated with a variety of materials to form devices. Recently, the use of self-assembled organic monolayers deposited on epitaxial graphene (prepared by graphitization of the 6H-SiC(0001) surface) has been effective in the functionalization of the bare graphene sheet, enabling the additional chemistry necessary for device fabrication. In this work, we present high-resolution X-ray Reflectivity (XRR) studies of perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA) on epitaxial graphene. Initially, a model-independent vertical electron density profile of the graphene/silicon carbide interface is retrieved with the use of Feinup-based error correction algorithms in order to minimize ambiguities that can arise from model-based methods. This retrieved structure is then used as the foundation for model-based analysis, from which the final structures are extracted. A series of structures comprising 0, 1, and 2MLs of PTCDA deposited on 1-2ML graphene are discussed. The interlayer spacing between the PTCDA and top graphene layer are revealed to be approximately 0.35 nm, which supports the view that the PTCDA molecules are interacting only weakly (van der Waals) with the graphene layer. In addition to the characterization of PTCDA-functionalized graphene, we will also demonstrate the efficacy of these molecules to form a weakly-interacting seeding layer for subsequent growth of high-k dielectrics via atomic layer deposition.

8:20am **GR+AS+BI+PS+SS-WeM2 *In Situ* FT-IR Study of Graphene Fluorination using XeF_2**, ***J.-F. Veyan***, *N. Shafiq,* University of Texas at Dallas*, K. Novoselov,* University of Manchester, UK*, Y.J. Chabal*, University of Texas at Dallas

Graphene fluorination to obtain fluorographene has been successfully realized by exposing graphene flakes to molecular Xenon-Difluroride [1-3]. To gain a mechanistic understanding of XeF_2 reaction with the graphene flakes, an all-aluminum custom-made two-stage reaction cell has been designed to fit into the main sample compartment of an FTIR Nicolet 6700 interferometer, for *in situ* infrared absorption spectroscopy. The first stage is a clean expansion chamber to isolate the pure XeF_2 in its gas phase, from solid XeF_2 (powder) stored in a storage vessel. The XeF_2 vapor is extracted by opening the valve V1 to the storage chamber and its pressure (up to ~4 Torr) is controlled by the valve V2. The second stage is a reactor equipped with two KBr windows, allowing the IR beam to penetrate and exit the enclosure. A pneumatic valve allows the transfer of gaseous XeF_2 from stage 1 into stage 2. Pressures in both storage and reactor chambers are measured with Baratron gauges (Ga1, Ga2). To avoid any contamination of the reactor and sample holders during sample preparation and loading, a N_2-purged glove bag is placed over the reactor to maintain a controlled environment. The graphene flakes in suspension in a NMP (N-Methylpyrrolidon) solution, are transferred onto three mechanically polished Aluminum plates at a temperature of 70°C. The plates are then mounted on the specially designed 3-reflection sample holder flange designed to fit stage 2.

By varying the sample temperature from 20 to 200°C as well as the XeF2 pressure in the reactor stage from 0.1 to 4 Torr, the chemical attachment of fluorine on graphene is identified from a comprehensive FT-IR study performed under under industrial conditions. Fluorine attached out of plane can be easily differentiated from fluorine attached at edges (i.e. remaining within the basal plane) and terminating the edge atoms.

[1] R. R. Nair, et al., Small **6**, 2877 (2010).

[2] J. T. Robinson, et al., Nano Letters **10**, 3001 (2010).

[3] K.-J. Jeon, et al., Acs Nano **5**, 1042 (2011).

8:40am **GR+AS+BI+PS+SS-WeM3 Molecularly Resolved Chemical Functionalization of Graphene**, ***M.C. Hersam***, Northwestern University **INVITED**

Graphene has emerged as one of the leading materials in condensed matter physics due to its superlative electrical and mechanical properties. With an eye towards expanding its functionality and applications, this talk will highlight our latest efforts to tailor the surface chemistry of graphene [1]. At the molecular scale, we employ ultra-high vacuum (UHV) scanning tunneling microscopy (STM) and conductive atomic force microscopy (cAFM) to characterize chemically modified epitaxial graphene on SiC(0001) [2,3]. For example, a suite of perylene-based molecules form highly ordered self-assembled monolayers (SAMs) on graphene via gas-phase deposition in UHV [4,5]. Due to their noncovalent bonding, these SAMs preserve the superlative electronic properties of the underlying graphene while providing uniform and tailorable chemical functionality [6]. In this manner, disparate materials (e.g., high-*k* gate dielectrics) can be seamlessly integrated with graphene, thus enabling the fabrication of capacitors, transistors, and related electronic/excitonic devices [7]. Alternatively, via aryl diazaonium chemistry, functional polymers can be covalently grafted to graphene [8], while exposure to atomic oxygen in UHV enables chemically homogeneous and thermally reversible covalent epoxy functionalization [9]. Beyond UHV STM characterization, this talk will also delineate our most recent efforts to exploit chemically modified graphene in technologically significant applications including photovoltaics [10], transparent conductors [11-13], flexible GHz transistors [14], *in vivo* biomedical applications [15,16], and photocatalysts [17].

[1] Q. H. Wang and M. C. Hersam, *MRS Bull.*, **36**, 532 (2011).

[2] J. A. Kellar et al., *Appl. Phys. Lett.*, **96**, 143103 (2010).

[3] J. M. P. Alaboson et al., *Adv. Mater.*, **23**, 2181 (2011).

[4] Q. H. Wang and M. C. Hersam, *Nature Chemistry*, **1**, 206 (2009).

[5] Q. H. Wang and M. C. Hersam, *Nano Lett.*, **11**, 589 (2011).

[6] J. D. Emery et al., *Surf. Sci.*, **605**, 1685 (2011).

[7] J. M. P. Alaboson, et al., *ACS Nano*, **5**, 5223 (2011).

[8] Md. Z. Hossain et al., *J. Am. Chem. Soc.*, **132**, 15399 (2010).

[9] Md. Z. Hossain et al., *Nature Chemistry*, **4**, 305 (2012).

[10] I. P. Murray et al., *J. Phys. Chem. Lett.*, **2**, 3006 (2011).

[11] A. A. Green and M. C. Hersam, *J. Phys. Chem. Lett.*, **1**, 544 (2010).

[12] A. A. Green and M. C. Hersam, *Nano Lett.*, **9**, 4031 (2009).

[13] Y. T. Liang and M. C. Hersam, *J. Am. Chem. Soc.*, **132**, 17661 (2010).

[14] C. Sire et al., *Nano Lett.*, **12**, 1184 (2012).

[15] M. C. Duch et al., *Nano Lett.*, **11**, 5201 (2011).

[16] J.-W. T. Seo et al., *J. Phys. Chem. Lett.*, **2**, 1004 (2011).

[17] Y. T. Liang et al., *Nano Lett.*, **11**, 2865 (2011).

9:40am **GR+AS+BI+PS+SS-WeM6 Structure of a Peptide Adsorbed on Graphene and Graphite**, *J. Katoch,* University of Central Florida*, S.N. Kim, Z. Kuang, B.L. Farmer, R.R. Naik,* Air Force Research Laboratory*, S.A. Tatulian,* ***M. Ishigami***, University of Central Florida

Non-covalent functionalization of graphene using peptides is a promising method for producing novel sensors with high sensitivity and selectivity. We have performed atomic force microscopy, Raman spectroscopy, infrared spectroscopy and molecular dynamics simulations to investigate peptide-binding behavior to graphene and graphite. We studied a dodecamer peptide, GAMHLPWHMGTL, identified by phage display to possess affinity for graphite.

Optical spectroscopy reveals that the peptide forms secondary structures both in powder form and in an aqueous medium. The dominant structure in the powder form is α-helix, which undergoes a transition to a distorted helical structure in aqueous solution. The peptide forms a complex reticular structure upon adsorption on graphene and graphite, having a helical conformation different from α-helix due to its interaction with the surface. Our observation is consistent with our molecular dynamics calculations and our study paves way for rational functionalization of graphene using

biomolecules with defined structures and, therefore, functionalities. Our results have recently been published [1].

[1] J. Katoch, S.N. Kim, Z. Kuang, B. L. Farmer, R. R. Naik, S. A. Tatulian, and M. Ishigami, dx.doi.org/10.1021/nl300286k, Nano Letters (2012).

10:40am **GR+AS+BI+PS+SS-WeM9 Controlling the Spatial Distribution of Graphene Chemistry**, ***S.C. Hernández***, *E.H. Lock, S.G. Walton, C.J. Bennett, R. Stine, P.E. Sheehan, F.J. Bezares, L.O. Nyakiti, R.L. Myers-Ward, J.T. Robinson, J.D. Caldwell, C.R. Eddy, Jr., D.K. Gaskill*, Naval Research Laboratory

Graphene has attracted a widespread of interest because of its unique structural and electronic properties however, manipulation of these properties is necessary before realizing its full potential as the next generation material in a broad range of applications. Precise control of the surface chemistry of graphene can allow for subsequent surface procedures both for device fabrication (i.e. atomic layer deposition) and sensor applications. Chemical composition strongly impacts the electronic properties as well as chemical reactivity, both globally and locally. Electron-beam generated plasmas are capable of imparting a variety of functional group types over a range of coverages with minimal damage to the carbon back bone because of their inherently low ion energies and as such offer a unique approach for large area uniform processing of graphene films with controlled surface chemistry. The ability to manipulate the surface chemistry of this atomically thin material coupled with the capability to regulate the spatial distribution of functional will be discussed. Plasma processing conditions and characteristics, as well as the resulting chemical, structural, and electrical properties of the functionalized graphene will be demonstrated. This work is supported by the Naval Research Laboratory base program.

11:00am **GR+AS+BI+PS+SS-WeM10 Coverage-dependent Ordering of Adsorbed Iron Phthalocyanine on Epitaxial Graphene Grown on SiC(0001)-Si**, ***A.A. Sandin***, *D.B. Dougherty, J.E. Rowe*, North Carolina State University

The crystallographic and electronic structure of monolayer and sub-monolayer Iron-Phthalocyanine (FePc) films are experimentally studied on graphene grown on SiC(0001) using Scanning Tunneling Microscopy and Spectroscopy (STM and STS) as well as Low Energy Electron Diffraction (LEED). At full monolayer coverage of FePc the STM images show that a nearly square overlayer lattice forms with flat-lying molecules and a densely-packed structure oriented 10° relative to the graphene principle lattice directions. This close-packed structure i appears to be the same as that previously reported for FePc on graphite surfaces. For sub-monolayer coverage at room temperature, our STM images suggest that FePc forms a unique 2D molecular gas with images that have the hexagonal symmetry of the graphene honeycomb lattice. This is interpreted as suggesting that only a small diffusion barrier exists for molecular motion between neighboring sites in the 3-fold symmetry of the sub-monolayer overlayer lattice. The sub-monolayer gas condenses into islands at liquid Nitrogen temperatures with bare graphene regions and this implies that a weak attractive interaction exists between FePc molecules causing the close-packed ordering. Near defects in the graphene lattice we observe ring-like structures at room temperature that suggest an increased residence time of the mobile 2-D gas of FePc molecules. Our results using Scanning Tunneling Spectroscopy suggest the possibility of a hybrid molecule-graphene state in the unoccupied density of both states near the Fermi level which could possibly be useful in modifying the charge injection into graphene in future devices.

11:20am **GR+AS+BI+PS+SS-WeM11 A Molecular Route to Carbon Nanomembranes, Graphene and Their Hybrids with Tailored Physical and Chemical Properties**, ***A. Turchanin***, University of Bielefeld, Germany **INVITED**

Bottom-up approaches via molecular self-assembly have high potential to facilitate the applications of two-dimensional (2D) carbon materials in nanotechnology. In this talk it will be demonstrated how self-assembled monolayers (SAMs) of aromatic molecules can be employed to this end. These monolayers are converted into *carbon nanomembranes* (CNMs) with a thickness of one molecule by electron or photon irradiation. CNMs can be separated from their original substrates and transferred onto various other substrates, fabricated as suspended nanomembranes or stacked into multilayer films with precise control over their thickness and composition. They possess two chemically distinct faces, which can be used for their selective functionalization, opening broad avenues for the engineering of novel materials with tailored on demand properties. High temperature annealing induces the transformation of CNMs into *graphene*, which allows large-area fabrication of the homogenous sheets with tunable electrical, optical and chemical properties. Integration of graphene sheets with CNMs into novel hybrids presents a promising route to flexibly functionalize graphene for applications as optical, electrical, chemical and biofunctional coating in nanoelectronics and sensors. Various physical and chemical properties of these novel materials, their nanopatterning and functional applications will be presented.

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Scanning Probe Microscopy Focus Topic
Room: 16 - Session SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM

Probe-Sample Interactions, Nano-Manipulation and Fabrication

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

8:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM2 Controlled Coupling of Silicon Atomic Quantum Dots at Room Temperature: A Basis for Atomic Electronics?**, ***R.A. Wolkow***, University of Alberta and The National Institute for Nanotechnology, Canada, *J. Pitters,* The National Institute for Nanotechnology, Canada, *G. DiLabio, M. Taucer, P. Piva, L. Livadaru*, University of Alberta and The National Institute for Nanotechnology, Canada **INVITED**

Quantum dots are small entities, typically consisting of just a few thousands atoms, that in some ways act like a single atom. The constituent atoms in a dot coalesce their electronic properties to exhibit fairly simple and potentially very useful properties. It turns out that collectives of dots exhibit joint electronic properties of yet more interest. Unfortunately, though extremely small, the finite size of typical quantum dots puts a limit on how close multiple dots can be placed, and that in turn limits how strong the coupling between dots can be. Because inter-dot coupling is weak, properties of interest are only manifest at very low temperatures (milliKelvin). In this work the ultimate small quantum dot is described – we replace an "artificial atom" with a true atom - with great benefit.

It is demonstrated that the zero-dimensional character of the silicon atom dangling bond (DB) state allows controlled formation and occupation of a new form of quantum dot assemblies - at room temperature. Coulomb repulsion causes DBs separated by less than ~2 nm to experience reduced localized charge. The unoccupied states so created allow a previously unobserved electron tunnel-coupling of DBs, evidenced by a pronounced change in the time-averaged view recorded by scanning tunneling microscopy. It is shown that fabrication geometry determines net electron occupation and tunnel-coupling strength within multi-DB ensembles and moreover that electrostatic separation of degenerate states allows controlled electron occupation within an ensemble.

Some speculation on the viability of a new "atomic electronics" based upon these results will be offered.

9:00am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM4 Atomic Forces and Energy Dissipation of a Bi-Stable Molecular Junction**, ***C. Lotze***, Freie Universtiät Berlin, Germany, *M. Corso, K.J. Franke, F.V. Oppen, J.I. Pascual*, Freie Universität Berlin, Germany

Tuning Fork based dynamic STM/AFM is a well established method combining the advantages of scanning tunneling and dynamic force microscopy. Using tuning forks with high stiffness, stable measurements with small amplitudes, below 1 Å can be performed. In this way, conductance and frequency shift measurements of molecular junction can be obtained simultaneously [1] with intramolecular resolution [2].

One of the most intriguing aspects of molecular junctions relates to the effect of structural bi-stabilities to the properties of the junction. These lead,

for example, to conductance fluctuations, telegraph noise and the possibility to switch the electrical transport through the junction.

In this presentation, we characterize a model bi-stable molecular system using dynamic force spectroscopy. The effect of current-induced stochastic fluctuations of conductance are correlated with fluctuations in force. In our experiment we identified the last from both, frequency shifts and energy dissipation measurements, picturing a regime in which electrical transport and mechanical motion are coupled.

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9:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM5 Acetylene on Cu(111): Imaging a Molecular Pattern with a Constantly Rearranging Tip**, ***Y. Zhu***, *J. Wyrick, K.D. Cohen, K. Magnone, C. Holzke, D. Salib, Q. Ma, D.Z. Sun, L. Bartels*, University of California Riverside

Abstract: Using variable temperature STM and DFT simulation, we identify the phases of acetylene adsorbed on the Cu(111) surface. Depending on the coverage, a diffraction-derived surface pattern of acetylene on Cu(111) is validated by STM. The modification of the STM image transfer function through the adsorption of an acetylene molecule onto the tip apex is taken into account. In this case, the images of acetylene patterns on Cu(111) also include direct evidence of **the rotational orientation and dynamics of the acetylene species attached to the tip apex**. DFT modeling of acetylene/Cu(111) reveals that the molecular orientation and separation is governed by a balance of repulsive interactions associated with stress induced in the top surface layer and attractive interactions mediated by the electronic structure of the substrate. Computationally modeling of the substrate with 3 layers obtains the periodicity of the intermolecular interaction that provides a theoretical underpinning for the experimentally observed molecular arrangement.

9:40am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM6 Atomic Scale Imaging and Electronic Structure of Trimethylaluminum Deposition on III-V Semiconductor (110) Surfaces**, ***T.J. Kent****, *M. Edmonds, E. Chagarov, A.C. Kummel*, University of California San Diego

Silicon based metal oxide semiconductor field effect transistors (Si-MOSFETs) are quickly approaching their theoretical performance limits, as a result many semiconductors are being explored as an alternative channel material for use in MOSFETs. III-V semiconductors are an appealing alternative to Si because of their higher electron mobilities. The limiting factor in III-V based MOSFET performance is defect states which prevent effective modulation of the Fermi level. The InGaAs (001) As-rich (2x4) surface contains two types of unit cells: ideal unit cells with double As-dimers and defect unit cells with single As-Dimers. The missing As-dimer unit cells, which comprise ~50% of the surface, are believed to cause electronic defect states at the semiconductor-oxide interface, specifically at the conduction band edge of the semiconductor. *In-situ* scanning tunneling microscopy and spectroscopy (STM/STS) and density function theory (DFT) modeling show that TMA readily passivates the As-As dimers in the ideal unit cell but the missing InGaAs(001)-2x4 may not be fully passivated by TMA. To improve the electronic structure of the interface, the sidewalls of the finFETs on InGaAs(001) can be fabricated along the (110) direction. The (110) surface contains only buckled III-V heterodimers in which the lower group III atom is sp2 hybridized with an empty dangling bond and the upper group V atom is sp3 hybridized with a full dangling bond. This results in an electrically unpinned surface.

To investigate the benefits of using a (110) surface as a channel material, the atomic and electronic structure of the ALD precursor trimethylaluminum (TMA) monolayer deposited on III-V (110) surfaces has been studied using *in-situ* STM and STS. Both GaAs and InGaAs samples were studied. GaAs wafers were obtained from Wafertech with a Si doping concentration of 4x1018/cm3. The (001) samples were cleaved *in-situ* to expose the (110) surface. Samples were transferred to the STM chamber (base pressure 1x10-11 torr) where the atomic bonding structure of the precursor monolayer unit cell was determined. STS, which probes the local density of states (LDOS), was used to determine Fermi level pinning. A model of TMA chemisorption was developed in which TMA chemisorbs between adjacent As atoms on the surface, giving a highly ordered monolayer with a high nucleation density which could allow for aggressive effective oxide thickness (EOT) scaling.

10:40am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM9 A New Experimental Method to Determine the Torsional Spring Constants of Microcantilevers**, ***G. Haehner***, *J.D. Parkin*, University of St Andrews, UK

Cantilever based technologies have seen an ever increasing level of interest since the atomic force microscope (AFM) was introduced more than two decades ago. Recent developments employ microcantilevers as stand-alone sensors by exploiting the dependence of their oscillating properties on external parameters such as adsorbed mass [1], or the density and the viscosity of a liquid environment [2,3]. They are also a key part in many microelectromechanical systems (MEMS) [4]. In order to quantify measurements performed with microcantilevers their stiffness or spring constants have to be known. Following calibration of the spring constants a change in oscillation behavior can be quantitatively related to physical parameters that are probed. The torsional modes of oscillation have attracted significant attention due to their high sensitivity towards lateral and friction forces, and recent developments in torsional-tapping AFM technology [5]. However, the methods available to determine the torsional spring constants experimentally are in general not simple, not very reliable, or risk damage to the cantilever [6].

We demonstrate a new method to determine the spring constants of the torsional modes of microcantilevers experimentally with high accuracy and precision. The method is fast, non-destructive and non-invasive. It is based on measuring the change in the resonance frequencies of the torsional modes as a function of the fluid flow escaping from a microchannel. Results for rectangular cantilevers will be presented and compared to results obtained with other methods [7].

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11:00am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM10 A Torsional Device for Easy, Accurate and Traceable Force Calibration of AFM Cantilevers**, ***J.F. Portoles***, *P.J. Cumpson*, Newcastle University, UK

Accurate measurement of biologically-relevant forces in the range of pN to μN is an important problem in nanoscience.

A number of force probe techniques have been applied in recent years. The most popular is the Atomic Force Microscope (AFM). Accuracy of force measurement relies on calibration of the probe stiffness which has led to the development of many calibration methods[1], particularly for AFM microcantilevers. However these methods typically exhibit uncertainties of at best 15% to 20% and are often very time consuming. Dependency on material properties and cantilever geometry further complicate their application and take extra operator time. In contrast, one rapid and straightforward method involves the use of reference cantilevers (the "cantilever-on-cantilever" method) or MEMS reference devices. This approach requires that a calibrated reference device is available, but it has been shown to be effective in providing measurement traceability[2].

The main remaining difficulty of this approach for typical users is the positional uncertainty of the tip on the reference device, which can introduce calibration uncertainties of up to around 6%. Here we present a new reference device based on a torsional spring of relatively large dimensions compared to the typical AFM cantilever and demonstrate how it is calibrated. This method has the potential to calibrate the reference device traceably[3] to the SI with a 1% accuracy by applying techniques typically used for the characterisation of micromechanical devices. The large dimensions of the device reduce the positional uncertainty below 1% and simultaneously allow the use of the device as an effective reference array with different reference stiffnesses at different positions ranging from 0.090 N/m to 4.5 N/m

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***** ASSD Student Award Finalist

11:20am **SP+AS+BI+ET+MI+NM+NS+SS+TF-WeM11 Nanoscale Surface Assembly by Single-Molecule Cut-and-Paste**, ***H.E. Gaub***, Ludwig-Maximilians Universitat, Germany **INVITED**

Bottom up assembly of functional molecular ensembles with novel properties emerging from composition and arrangement of its constituents is a prime goal of nanotechnology. With the development of Single-Molecule Cut-and-Paste (SMC&P) we provided a platform technology for the assembly of biomolecules at surfaces. It combines the Å-positioning precision of the AFM with the selectivity of DNA hybridization to pick individual molecules from a depot chip and allows to arrange them on a construction site one by one. An overview on different applications of this technology will be given in this talk. One recent example demonstrates the functional of receptors for small molecules. By SMC&P we assembled binding sites for malachite green in a molecule-by-molecule assembly process from the two halves of a split aptamer. We show that only a perfectly joined binding site immobilizes the fluorophore and enhances the fluorescence quantum yield by several orders of magnitude. To corroborate the robustness of this approach we produced a micron-sized structure consisting of more than 500 reconstituted binding sites. To the best of our knowledge this is the first demonstration of a one by one bottom up functional bio-molecular assembly. Figure included in supplemental document. S. Kufer, Puchner E. M.,Gumpp H., Liedel T. & H. E. Gaub *Science* (2008), Vol 319, p 594-S. Kufer, Strackharn, M., Stahl S.W., Gumpp H., Puchner E. M. & H. E. Gaub *Nature Nanotechnology* (2009), Vol 4, p 45-M. Erdmann, R. David. A.N. Fornof, and H. E. Gaub, *Nature Chemistry* (2010), Vol 2, p 755-M. Strackharn, S. Stahl, E. Puchner & H.E. Gaub, *Nanoletters* (2012) in press

Scanning Probe Microscopy Focus Topic
Room: 16 - Session SP+AS+BI+ET+MI+TF-WeA

Emerging Instrument Formats

Moderator: A. Belu, Medtronic, Inc.

2:00pm **SP+AS+BI+ET+MI+TF-WeA1 Electrochemical Strain Microscopy: Nanoscale Imaging of Solid State Ionics**, ***S. Jesse***, Oak Ridge National Laboratory **INVITED**

Electrochemical reactions in solids underpin multiple applications ranging from electroresistive non-volatile memory and neuromorphic logic devices memories, to chemical sensors and electrochemical gas pumps, to energy storage and conversion systems including metal-air batteries and fuel cells. Understanding the functionality in these systems requires probing reversible (oxygen reduction/evolution reaction) and irreversible (cathode degradation and activation, formation of conductive filaments) electrochemical processes. Traditionally, these effects are studied only on the macroscopically averaged level. In this talk, I summarize recent advances in probing and controlling these transformations locally on nanometer level using scanning probe microscopy. The localized tip concentrates an electric field in a nanometer scale volume of material, inducing local ion transport. Measured simultaneously, the electromechanical response (piezo response) or current (conductive AFM) provides the information on bias-induced changes in a material. Here, I illustrate how these methods can be extended to study local electrochemical transformations, including vacancy dynamics in oxides such as titanates, LaxSr1-xCoO3, BiFeO3, and YxZr1-xO2. The formation of electromechanical hysteresis loops indistinguishable from those in ferroelectric materials illustrate the role ionic dynamics can play in piezoresponse force microscopy and similar measurements. In materials such as lanthanum-strontium cobaltite, mapping both reversible vacancy motion and vacancy ordering and static deformation is possible, and can be corroborated by post mortem STEM/EELS studies. The possible strategies for elucidation ionic motion at the electroactive interfaces in oxides using high-resolution electron microscopy and combined ex-situ and in-situ STEM-SPM studies are discussed. Finally, the future possibilities for probing electrochemical phenomena on in-situ grown surfaces with atomic resolution are discussed. This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

2:40pm **SP+AS+BI+ET+MI+TF-WeA3 Probing Electrochemical Phenomena in Reactive Environments at High Temperature: *In Situ* Characterization of Interfaces in Fuel Cells**, ***S.S. Nonnenmann***, *R. Kungas, J.M. Vohs, D.A. Bonnell*, University of Pennsylvania

Many strategies for advances in energy related processes involve high temperatures and reactive environments. Fuel cell operation, chemical catalysis, and certain approaches to energy harvesting are examples. Scanning probe microscopy provides a large toolbox of local and often atomic resolution measurements of phenomena at a scale that enables understanding of complex processes involved in many systems. Inherent challenges exist, however, in applying these techniques to the realistic conditions under which these processes operate. To overcome some of these challenges, we have designed a system that allows SPM at temperatures to 850° C in reactive gas environments. This is demonstrated with the characterization of an operating fuel cell. Solid oxide fuel cells (SOFCs) offer the highest conversion efficiencies with operating temperatures ranging from 400° C - 1000° C; and operate under variable gaseous fuel environments – H_2-based environments (anode side) and O_2-based environments (cathode side). Topography and the temperature dependence of surface potential are compared to impedance. While not (yet) at atomic levels of spatial resolution, these probes are at the scale to examine local interface properties.

3:00pm **SP+AS+BI+ET+MI+TF-WeA4 High-Resolution Scanning Local Capacitance Measurements**, ***M. Brukman***, University of Pennsylvania, *S. Nanayakkara,* National Renewable Energy Laboratory, *D.A. Bonnell*, University of Pennsylvania

Spatial variation of dielectric properties often dictates the behavior of devices ranging from field effect transistors to memory devices to organic electronics, yet dielectric properties are rarely characterized locally. We present methods of analyzing 2nd harmonic-based local capacitance measurements achieved through non-contact atomic force microscopy. Unlike contact-based methods, this technique preserves tip shape and allows the same probe to realize high-resolution topographic imaging and scanning surface potential imaging. We present an improved analysis of the electrical fields between tip and sample, yielding high sensitivity to the capacitance-induced frequency shift.

The techniques are applied to thin-film ceramics (SrTiO2 and HfO2), metals (Pt and Ti), and mixed-phase self-

assembled monolayers to illustrate application over all orders of dielectric constant. Conversion from frequency shift signal to dielectric constant κ is demonstrated, with sub-5 nm spatial resolution and dielectric constant resolution between 0.25 and 1.

4:00pm **SP+AS+BI+ET+MI+TF-WeA7 Experimental Calibration of the Higher Flexural Modes of Microcantilever Sensors**, ***J.D. Parkin***, *G. Hähner*, University of St Andrews, UK

Microcantilevers are widely employed as probes not only in atomic force microscopy [1], but also as sensors for mass [2], surface stress [3], chemical identification [3], or in measuring viscoelastic properties of cells [4].

Use of the higher flexural modes of microcantilever sensors is an area of current interest due to their higher Q-factors and greater sensitivity to some of the properties probed [2]. A pre-requirement for their exploitation, however, is knowledge of their spring constants [5]. None of the existing cantilever calibration techniques can calibrate the higher flexural modes easily.

We present a method that allows for the determination of the spring constants of all flexural modes. A flow of gas from a microchannel interacts with the microcantilever causing a measurable shift in the resonance frequencies of all flexural modes [6]. The method is non-invasive and does not risk damage to the microcantilever. From the magnitude of the frequency shifts the spring constants can be determined with high accuracy and precision. Experimental data for the response of the first four flexural modes of microcantilever beams used in AFM with spring constants in the range of ~0.03-90 N/m will be presented.

The spring constants of the first mode determined using our method are compared to those obtained with the Sader method [7]. Finite element analysis computational fluid dynamics (CFD) simulations of the experimental setup are used to provide an insight into the interaction of the flow with the microcantilever.

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4:20pm **SP+AS+BI+ET+MI+TF-WeA8 Atomic Imaging with Peak Force Tapping**, *B. Pittenger, Y. Hu, C. Su, S.C. Minne,* Bruker AFM, ***I. Armstrong***, Bruker Nano Surfaces Division

As its name implies, Atomic Force Microscopy (AFM) has long been used to acquire images at the atomic scale. However these images usually only show the lattice of atoms in the crystal and do not show individual atomic defects. In order to achieve atomic resolution, researchers have typically had to design their systems for the ultimate in noise performance, sacrificing ease of use, flexibility, and scan size. Recently we have demonstrated that, by using Peak Force Tapping, our large sample platforms (Dimension Icon, Dimension FastScan) are capable of obtaining atomic resolution imaging along with maps of the tip-sample interaction. Unlike standard TappingMode, or FM-AFM, Peak Force Tapping uses instantaneous force control, allowing the system to be insensitive to long range forces while maintaining piconewton level control of the force at the point in the tapping cycle that provides the highest resolution – the peak force. Since the modulation frequency is far from resonance, the technique is less sensitive to the cantilever thermal noise (Brownian motion). In addition to topography, this technique can provide maps of the interaction between the tip and the sample. This is possible since Peak Force Tapping has access to the instantaneous force between tip and sample at any point in the modulation cycle. To study the details of a tip-sample interaction, Atomic Peak Force Capture can acquire the entire force distance curve used to create the interaction maps. These curves can be exported for easy analysis with models of tip-sample interaction. In this talk we will discuss the latest atomic resolution results using Peak Force Tapping and the

implications of this with regard to studies of dissolution, crystallization, ordered liquids, and corrosion.

4:40pm **SP+AS+BI+ET+MI+TF-WeA9 Nanoscale Chemical Composition Mapping with AFM-based Infrared Spectroscopy**, *C.B. Prater, M. Lo, Q. Hu,* Anasys Instruments, *C. Marcott,* Light Light Solutions, *B. Chase,* University of Delaware, *R. Shetty, K. Kjoller,* ***E. Dillon***, Anasys Instruments **INVITED**

The ability to identify material under an AFM tip has been identified as one of the "Holy Grails" of probe microscopy. While AFM can measure mechanical, electrical, magnetic and thermal properties of materials, until recently it has lacked the robust ability to chemically characterize unknown materials. Infrared spectroscopy can characterize and identify materials via vibrational resonances of chemical bonds and is a very widely used analytical technique. We have successfully integrated AFM with IR spectroscopy (AFM-IR) to obtain high quality infrared absorption spectra at arbitrary points in an AFM image, thus providing nanoscale chemical characterization on the sub-100 nm length scale. Employing the AFM-IR technique, we have mapped nanoscale chemical, structural and mechanical variations in multilayer thin films, nanocomposites, polymer blends, organic photovoltaics, and biological materials including hair, skin, and bacterial and mammalian cells. Light from a pulsed infrared laser is directed at a sample, causing rapid thermal expansion of the sample surface at absorbing wavelengths. The rapid thermal expansion creates an impulse force at the tip, resulting in resonant oscillations of the AFM cantilever. The amplitude of the cantilever oscillation is directly related to the infrared absorption properties of the samples, enabling measurements of IR absorption spectra far below the conventional diffraction limit. AFM-IR can be used both to obtain point spectra at arbitrary points and to spatially map IR absorption at selected wavelengths. Simultaneous measurement of the cantilever's contact resonance frequency as excited by the IR absorption provides a complimentary measurement of relative mechanical properties. We have used these techniques to chemically identify individual chemical components in polymer nanocomposites and multilayer films and performed subcellular spectroscopy and chemical imaging on biological cells. Using self-heating probes we have been able to locally modify the state of a semicrystalline polymer and observe the resulting change in absorption spectra on the nanoscale. Using polarization sensitive AFM-IR, we have mapped spatial variations in molecular orientation in electrospun fibers.

5:20pm **SP+AS+BI+ET+MI+TF-WeA11 Quantifying Nanomechanical Properties with Simultaneous AM-FM and tanδ Imaging**, *T. Mehr,* ***A. Moshar***, *R. Proksch, I. Revenko, N. Geisse, S. Hohlbauch, D. Walters, J. Cleveland, J. Bemis, C. Callahan, D. Beck*, Asylum Research

Frequency-Modulated (FM) is a powerful, quantitative technique for mapping interaction forces between an oscillating tip and sample. Since FM-AFM typically requires the use of three feedback loops, one ongoing challenge has been stable and cross-talk free operation. Amplitude-modulated Atomic Force Microscopy (AM-AFM), also known as tapping mode, is a proven, reliable and gentle imaging method with wide spread applications. Recently, the phase signal of the first resonant mode has been recast in terms of the tip-sample loss tangent.[1] This allows quantitative imaging of a response term that includes both the dissipated and stored energy of the tip sample interaction. Combining AM and FM imaging allows reaping the benefits of both techniques.[2] Because the feedback loops are decoupled, operation is more robust and simple than conventional FM imaging. In this mode, the topographic feedback is based on the AM signal of the first cantilever resonance while the second resonance drive is frequency modulated. The FM image returns a quantitative value of the frequency shift that in turn depends on the sample stiffness and can be applied to a variety of physical models. We will present results on a wide variety of materials as well as discussing quantitative separation of the elastic and dissipative components of the tip-sample interactions.[3]

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5:40pm **SP+AS+BI+ET+MI+TF-WeA12 Simultaneous Scanning Tunneling and Atomic Force Microscopy with Subatomic Spatial Resolution**, ***FJ. Giessibl***, University of Regensburg, Germany

Frequency-modulation AFM can be combined with scanning tunneling microscopy, yielding a simultaneous data set for current and average force gradient. Ternes et al. [1] have shown that for some metallic contacts, force and current are proportional. The interaction of a tungsten tip with a CO molecule adsorbed on Cu(111), however, yields a much different symmetry and distance dependence of tunneling current and force [2]. The tunneling current yields a gaussian dip over the CO molecule, while the forces show a strong angular dependence with force fields that vary strongly by distance and angle within the extent of the single front atom, displaying subatomic variations. While the simultaneous acquisition of current and force can reveal new information about the atomic and electronic structure of matter, the tunneling current can modify the atomic forces. This “phantom force” [3,4], a modification of the electrostatic attraction between tip and sample, originates in an alteration of the effective potential difference between tip and sample caused by strongly localized voltage drop induced by the tunneling current. The talk discusses the potential of combined STM/AFM as well as the challenges, in particular with respect to tip preparation and characterization.

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Helium Ion Microscopy Focus Topic
Room: 19 - Session HI+AS+BI+NS-ThM

Imaging and Lithography with the Helium Ion Microscope

Moderator: A. Gölzhäuser, University of Bielefeld, Germany, V.S. Smentkowski, General Electric Global Research Center

8:40am **HI+AS+BI+NS-ThM3 Helium Ion Microscopy of Photonic Structures in Biological Systems**, ***S.A. Boden***, *A. Asadollahbaik, H.N. Rutt, D.M. Bagnall*, University of Southampton, UK **INVITED**

The natural world is replete with examples of biological systems that have developed complex micro- and nano-scale structures to interact with light. Such structures, which include thin film multilayers, diffraction gratings, graded index layers and 2D and 3D photonic crystals, acting alone or in combination, allow the realization of a range of optical effects that would be impossible through the use of pigmentation alone. These effects range from the vivid iridescence observed on the skin of some species of bird, through the vibrant metallic sheen of some beetle species, to the dramatic interference patterns seen on the transparent wings of some species of fly. Lepidoptera (an order of insects that includes butterflies and moths) also provides a rich seam of examples of structural color ranging from the antireflective nipple arrays found on the eyes and wings of some species of moth to the photonic crystal structures producing vivid coloration on the wings of some butterfly species.

As these optical effects are a result of the scale of these structures being at or below that of visible light wavelengths, scanning electron microscopy (SEM) is often used to explore their form and to offer insights into their function. Recently, helium ion microscopy (HIM) has emerged as a surface imaging technique, similar to SEM but with the benefits of higher resolution and a larger depth of field. Here, HIM is used to probe the structures responsible for a number of optical effects observed in Lepidopterans. Images will be presented showing the fine details of the ribs and cross-ribs found on the highly-absorbing black ground wing scales of *Papilio ulysses* (Blue Mountain Butterfly) and the complex gyroid 3D photonic crystal structure observed underneath the top lamina on vividly green wing scales from *Parides sesostris* (Emerald-patched Cattleheart). Other examples will include the antireflective close-packed nipple array on the wings of *Cephonodes hylas* (Pellucid Hawk Moth), and cross-sections of the multilayer structures that make up the various colored wing scales of *Chrysiridia rhipheus* (Madagascan Sunset Moth).

The integrated electron flood gun on the helium ion microscope is employed to neutralize charge build-up, allowing samples to be imaged without the need of a conductive coating. This ensures that the natural surface itself is imaged at high resolution and details are not obscured by coating artefacts. In addition, by taking advantage of the large depth of field available with HIM, stereo pairs are generated to extract information on the three-dimensional nature of these structures.

9:20am **HI+AS+BI+NS-ThM5 Imaging of Carbon Nanomembranes (CNM) and Graphene with Helium Ion Microscopy**, ***H. Vieker***, *A. Beyer, A. Polina, A. Willunat, N.-E. Weber, M. Büenfeld, A. Winter, X. Zhang, M. Ai, A. Turchanin, A. Gölzhäuser*, Bielefeld University, Germany

We present a Helium Ion Microscopy (HIM) study of carbon nanomembranes (CNMs). CNMs are extremely thin (~1 nm) nanolayers consisting only of surface. They are made via cross-linking of self-assembled monolayers (SAMs) with large-area exposures of electrons, photons or helium ions and a subsequent transfer to suitable substrates. Patterned radiation exposures allow the fabrication of perforated nanomembranes, e.g., nanosieves. After annealing at temperatures above 800K, CNMs become conductive and eventually transform into graphene. HIM images of CNMs with different precursor molecules are shown, and images of graphene from SAMs are compared with the CVD grown graphene. Capabilities of the HIM imaging of freestanding CNMs and graphene will be discussed.

10:40am **HI+AS+BI+NS-ThM9 Dopant Contrast in Helium Ion Microscopy**, *Y. Chen, H. Zhang,* ***D. Fox***, *C.C. Faulkner, J. Wang, J. Boland, J. Donegan*, Trinity College, Ireland **INVITED**

Innovation in metrology is crucial to the future of semiconductor industry, since the miniaturization of transistors demands novel characterization technologies at and beyond the nanometre scale. Recent research has demonstrated that dopant contrast in the Helium-ion Microscope (HIM) is plausible and the HIM is a competitive platform for quantitative secondary-electron (SE) dopant mapping in terms of throughput, sensitivity, and resolution. However, the contrast mechanism of SE imaging is still debatable and it hinders further development of the technique. In this research, quantitative HIM dopant contrast of gallium-doped silicon samples has been investigated and compared with the contrast observed in a scanning electron microscope (SEM). Beam-sample interaction, signal general, as well as detection configuration have been considered via using a range of detectors in the two microscopes. It has been found that the Everhart-Thornley (E-T) secondary electron detector attached to HIM provides similar contrast to the images acquired from the InLens detector attached to SEM, while contrast reversal is observed with the SEM E-T detector. The contrast reversal also depends on the Dwell time. We have confirmed that the HIM is more sensitive to type-I SEs and a capacitance model based on charging effect has been proposed to explain the contrast reversal. Our results indicate that quantitative dopant contrast in the HIM is promising, while charging effect and imaging conditions must be carefully considered.

11:20am **HI+AS+BI+NS-ThM11 High Resolution Patterning of Carbon Nanomembranes and Graphene via Extreme UV Interference Lithography: A Helium Ion Microscopy Study**, ***A. Winter***, *A. Willunat, A. Beyer,* University of Bielefeld, Germany, *Y. Ekinci,* Paul Scherrer Institute, Switzerland, *A. Gölzhäuser, A. Turchanin*, University of Bielefeld, Germany

Two-dimensional (2D) carbon materials like graphene, graphene oxide, carbon nanomembranes (CNMs) or ultrathin polymeric films have recently attracted enormous interest due to their potential use in electronics, chemical and biological sensors, nanofilters, hybrid materials, etc. Most of these applications require lithographic patterning of these 2D carbon materials with the nanoscale resolution. In this respect, Extreme UV Interference Lithography (EUV-IL) provides both large-scale pattering and high resolution with an ultimate limit in the sub-10 nm range. We employ EUV-IL to generate nanopatterns in ~1 nm thick CNMs and graphene. We characterise these nanopatterns with a Helium Ion Microscope (HIM). Its high surface sensitivity and lateral resolution provide excellent conditions for imaging of the topographic and chemical features in CNMs and graphene. The possibility to routinely fabricate and characterize the nanopatterns via EUV-IL and HIM on various technologically relevant insulating substrates (e.g., oxidized silicon wafers, glass, and quartz) and with the resolution below 20 nm shows high potential of both techniques for applications in carbon-based nanotechnology.

11:40am **HI+AS+BI+NS-ThM12 Application of Helium Ion Microscope on Processing and Characterization of Nano Wires**, ***H.X. Guo***, *S. Nagano, K. Onishi, D. Fujita*, National Institute for Materials Science (NIMS), Japan

Scanning helium ion microscope (SHIM) is advanced in high resolution and high focal depth of secondary electron imaging and Rutherford backscattered ion imaging.[1] It also employed in the nano pattern or fabrication on surface and other various structures, such as 2D materials, graphene.[2] It is an excellent candidate for the naon processing of 1D nano structures, such as nanowires and nanotubes.

Rhenium trioxide (ReO3) is an unusual transition metal oxide with high electrical conductivity close to that of metals. It is well investigated for the applications of photovoltaics[3], catalyst[4],and tip for scanning tunneling microscope[5]. Various ReO3 nano structures such as nano paticles[3,6], nano wires[7], and core-shell structures have been synthesized and characterized by different methods.

In this research, ReO3 nanowires were synthesized by a physical vapor deposition method. Etched by the helium ion beam, the diameter of part of the nanowire was decreased. During this processing, the structure and transport properties of the ReO3 nanowire were modified with a controllable method. In this presentation, we will show the structure and properties characterization of the etched nanowires by using scanning probe microscope (SPM) , transmission electron microscope (TEM) and other methods. An *in-situ* transport properties measurement system with SHIM will also be introduced in the presentation.

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Biofilms and Biofouling: Marine Medical Energy Focus Topic
Room: 23 - Session MB+BI-ThM

Biofilms and Biofouling in Medicine
Moderator: L. Hanley, University of Illinois at Chicago

8:20am **MB+BI-ThM2 Simple and Versatile Approaches to Design Oligoethylene Based Self-Assembled Monolayers using Thiolene Chemistry on Different Metal Oxide Surfaces: Impact on Protein Adsorption**, ***A. Galtayries***, *A. Dellinger,* Chimie ParisTech (ENSCP), 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. An efficient method to control adsorption includes the use of well-defined oligo(ethylene glycol)-terminated self-assembled monolayer (SAM). However, multiple processing steps are often required to prepare SAM onto substrate. To address these problems of surface modification, we have developed a simple method using the powerful thiolene reaction to prepare self-assembled monolayer on different metal oxides to control bioadhesion on surfaces starting from commercially available building blocks, and taking the advantage of the photoreaction to easily create adhesive and anti-adhesive patterns.

Such well-controlled grafting strategy has been applied to different metal oxides: from silicon substrates for the methodology set-up to model metal oxides formed on biocompatible metals and alloys. The obtained films are robust; the process is low-cost, simple, and efficient.

Surface characterization 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) were used to check the surface composition at different steps of the reactions: the thiolene reaction, the PEG grafting, as well as after interaction with protein solutions: albumin for preliminary tests, and fibronectin, an adhesive protein present in the extra-cellular matrix. In addition to quantitative information, obtained by XPS, about the oxide composition and thickness at the different steps, and qualitative information, obtained by XPS and ToF-SIMS, surface patterning could be emphasized with ToF-SIMS chemical surface imaging.

8:40am **MB+BI-ThM3 Antibacterial Studies of Plasma Polymerised Cineole Thin Films**, ***A. Pegalajar-Jurado***, Swinburne University of Technology, Australia*, C.D. Easton,* CSIRO Materials Science and Engineering, Australia*, S.L. McArthur*, Swinburne University of Technology, Australia

Essential oils such as tea tree oil are known for their antibacterial properties. They have been used extensively as effective topical antimicrobial agents and are active against a wide range of micro-organisms. Traditionally, the antimicrobial properties of tea tree oil has been linked to the constituents of the oil including terpinen-4-ol and 1,8-cineole. To translate these antimicrobial properties into medical devices, methods for incorporating or coating materials are required. Recently, thin polymer films from terpinen-4-ol have been fabricated using plasma polymerisation. Initial data suggests that some antimicrobial activity was maintained. While plasma polymer films of 1,8-cineole have been fabricated previously, little focus has been placed on the antibacterial activity of this constituent.

The activity of 1,8-cineole against *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) was evaluated based on the time-kill approach. Several concentrations of the oil (0.05 %, 0.2 %, 0.3 % and 0.5 % v/v) were added to broth media containing $3x10^8$ CFU/mL of each bacterium. The optical density of the resulting solutions was measured at intervals over 24-hrs to monitor bacterial growth rates. The results demonstrated that concentrations above 0.35% v/v gave a 90% kill rate in the gram-negative *E. coli* after 8-hrs. Interestingly, the oil was less effective against the gram-positive *S. aureus*, producing a lower kill rate and rapid growth recovery in a 24-hour period.

Plasma polymers thin films of 1,8-cineole and 1,7-octadiene (hydrophobic control) were prepared using a stainless steel plasma reactor as described previously, while uncoated glass slides were used as a hydrophilic, positive control. Samples were then exposed to broth media containing $3x10^8$ CFU/mL of each bacteriumto determine the effects of the coatings on bacterial attachment and growth. In this work, bacterial studies of the coating behaviour have focused on the attachment of *S.aureus* and *E. coli*, and biofilm formation of *E. coli*. Comparison of the plasma polymerised cineole (ppCineole) coating with the two controls demonstrated a reduction in bacterial attachments over 18-hrs. The reduction in bacterial attachment was more obvious in the case of *E.coli* in comparison with *S. aureus*. There were not significant differences between plasma polymerised cineole and octadiene in the inhibition of *E.coli* attachment and growth over a period of 18-hours. However, the biofilm studies indicated that only the 1,8-cineole film demonstrated antimicrobial behaviour over a period of time of 5 days.

Keywords: plasma polymerisation, antibacterial activity, cineole

9:00am **MB+BI-ThM4 Robustness Analysis of Biofilm Antibiotic Tolerance**, ***R.P. Carlson***, Montana State University **INVITED**

Biofilms are ubiquitous and are thought to be involved in more than half of all medical infections. Even after decades of investigation, the *in vivo* efficacy of many antimicrobial strategies is still debated suggesting a need for better understanding of biofilm antimicrobial tolerances. The robustness of biofilm antibiotic tolerance to medically and industrially relevant culturing perturbations was characterized. By definition, robust systems return similar, predictable responses when perturbed while non-robust systems return very different and potentially unpredictable responses. Biofilm antibiotic tolerance was found to vary in unpredictable manners based on modest perturbations in culturing conditions. The predictability of an antibiotic tolerance response is essential to developing, testing, and employing antimicrobial strategies. The collective data represents both challenges and opportunities for the rational design of anti-biofilm strategies. The data demonstrates that biofilms can be countered effectively with some antibiotics if the appropriate environmental conditions are applied however, if inappropriate conditions are applied, the efficacy of the treatment can be negated. The results indicate it is essential to evaluate antimicrobial strategies over a range of perturbations relevant to the targeted application so accurate predictions regarding efficacy can be made. In addition, the highly dynamic antibiotic tolerance responses observed here may explain why some current antimicrobial strategies occasionally fail.

9:40am **MB+BI-ThM6 Analysis of Force Curves of *Pseudomonas Aeruginosa* obtained by Atomic Force Microscopy**, *E.V. Anderson, R.L. Gaddis, T.A. Camesano,* ***N.A. Burnham***, Worcester Polytechnic Institute

Pseudomonas aeruginosa is extremely harmful to immune-compromised individuals. An atomic force microscope (AFM) can be used to measure the forces between the AFM tip and the bacterial exopolymers, with which the bacteria attach themselves to surfaces. These forces are characterized with a model that is a function of brush (exopolymer) layer thickness, probe radius, temperature, separation distance, and a molecular volume. Initial experiments with limited data sets are consistent with expected brush thicknesses of a few hundred nanometers. In order to progress – now with rigor – we have just developed a high throughput method for the analysis of force curves on the exopolymers of *P. aeruginosa* [1]. The above-described model is only valid for the region where the tip is in contact with the exopolymers, yet is not perturbing the bacterial membrane. MatLab code was written to determine the location of this region in each force curve, crop the curve to that region, and apply the force model in order to obtain parameters of the exopolymers. The standard deviation of the mean and Chauvenet's Criterion are then applied to the results of sets of one-hundred force curves to increase measurement precision and objectively remove outliers. This procedure removes user subjectivity in cropping, fitting, and outlier removal, decreases analysis time by two orders of magnitude, and increases the precision of fitted results by a factor of ten (for one-hundred curves), which is necessary for demonstrating the statistical significance of our data.

[1] Anderson et al., to be submitted May 2012.

10:40am **MB+BI-ThM9 Light and Dark Biocidal Activity of Conjugated Polyelectrolytes**, ***K. Schanze***, University of Florida*, D.G. Whitten, T. Corbitt, E. Ji, D. Dascier,* University of New Mexico*, A. Parthasarathy, S. Goswami*, University of Florida **INVITED**

Cationic conjugated polyelectrolytes (CPEs) are semiconducting organic polymers that contain ionic solubilizing groups. These polymers are soluble in water and they self-assemble into colloidal nanostructures in solution and layer-by-layer films at interfaces. CPEs interact strongly with bacteria in solution and on coated interfaces, and under short wavelength visible or near UV light irradition they exhibit strong biocidal activity. Mechanistic studies using photophysics and cell live/dead assays find that the CPEs

efficiently sensitize the production of singlet oxygen, and this is believed to be at least partially responsible for the light-activated biocidal activity. Structure-property studies find that specific hydrophobic CPEs exhibit strong dark biocidal activity. Studies with membrane models indicate that the dark active CPEs exhibit a strong tendency to interact with and disrupt the cell membrane structure.

11:20am **MB+BI-ThM11 Mechanisms of Antimicrobial Activity of Quaternary Ammonium Compounds in Solution and Immobilized on a Surface**, ***H.C. Van der Mei***, University Medical Center Groningen, The Netherlands

Quaternary ammonium compounds (QAC) are potent cationic antimicrobials used in everyday consumer products like contact lens solutions and mouthrinses as well as in numerous industrial processes, like water purification. Unlike the case for many antibiotics, the development of bacterial resistance against QACs is considered unlikely, although *Pseudomonas aeruginosa* strains isolated from contact lens cases have been shown to possess resistance against QACs. The first step in the antimicrobial action of QACs is the approach of the QAC molecule towards the bacterial cell surface. This is mediated by hydrophobic and electrostatic attractions between positively charged QAC molecules and the negatively charged bacterial cell surface. Upon their subsequent adsorption, QAC molecules replace Ca^{2+} or Mg^{2+} ions from the cytoplasmic membrane in order to maintain charge neutrality in the membrane. The replacement of Ca^{2+} and Mg^{2+} ions by QACs destabilizes the intracellular matrix of a bacterium, as the hydrophobic tail interdigitates into the hydrophobic bacterial membrane causing leakage of intracellular fluid and loss of turgor pressure. Antimicrobial efficacy of QACs remains preserved when QAC molecules are immobilized on a substratum surface. It is difficult to envisage how immobilized QAC molecules can exert the same mechanism of antimicrobial activity as do QACs in solution. Immobilized QACs, especially after adsorption of a protein film as developing rapidly in the human body, are strongly hindered in their search for heterogeneously distributed negative charges on bacterial cell surfaces which is crucial for their efficacy in solution. Hence, it has been often hypothesized that QAC molecules immobilized to a substratum surface possess other generic mechanisms of action than QACs in solution, but these have never been elucidated. Immobilized QACs do not cause directly visual membrane damage. Instead, the strong adhesion forces arising from immobilized QACs enter bacterial adhesion forces into the lethal regime, i.e. where the stress exerted on the bacterial cell membrane is causing killing.

11:40am **MB+BI-ThM12 Combinatorial Discovery of Materials That Resist Bacterial Adhesion**, ***A.L. Hook***, *C. Chang, J. Yang,* University of Nottingham, UK, *R. Langer, D.G. Anderson,* Massachusetts Institute of Technology, *S. Atkinson, P. Williams, M.C. Davies, M.R. Alexander*, University of Nottingham, UK

Biofilm formation leads to a 1000 times increase in antibiotic tolerance compared with planktonic bacteria and is associated with 80% of hospital acquired infections, resulting in $3.0 billion in excess health-care costs each year in the U.S alone. Thus, new materials that prevent biofilm formation would offer enormous benefits to the health industry and improve patient welfare. However, the limited understanding of bacteria-material interactions restricts the rational design of such materials. Polymer microarrays are emerging as a key enabling technology for the discovery of new biomaterials[1] and have been utilised to identify novel polymers that resist bacterial attachment.

Polymer microarrays were formed as previously described.[2] This platform enabled a large combinatorial space to be rapidly screened by a biological assay to identify new materials that fulfil a given performance criterion.[3] In the present study a bacterial attachment assay was developed using green fluorescing protein (GFP) tagged bacterial strains (*Pseudomonas aeruginosa, Staphylococcus aureus and Escherichia coli)* where the attachment of bacteria to each material was quantified by measuring the fluorescnce after incubation for 72 h.

Due to the large combinatorial chemical space available to the polymer micoarray format a strategy was devised to rapidly identify the optimal polymer composition that resists bacterial adhesion. This utilised a multi-generation microarray approach where the 'hits' from one array feed into the design of a subsequent array. Initially, an array was formed from 22 monomers with varied chemistry that were mixed to form 488 unique material compositions. Hit compositions were chosen from this array to produce a focussed second generation array containing unique materials where the hit compositions were varied incrementally. The resulting hit compositions were all amphiphilic containing both hydrophobic and hydrophilic moieties.

A methodology has been developed to screen the vast combinatorial chemical space within polymer chemistry for optimised compositions that produce novel materials with inherent resistance to bacterial adhesion. Key to this approach was the use of multi-generation microarrays.

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Biofilms and Biofouling: Marine Medical Energy Focus Topic
Room: 23 - Session MB+BI-ThA

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

2:00pm **MB+BI-ThA1 The Role of Oxygen in Microbiologically Influenced Marine Corrosion**, ***B.J. Little***, *J.S. Lee, R.I. Ray*, Naval Research Laboratory **INVITED**

Two microbiologically mediated processes dominate the literature on microbiologically influenced corrosion (MIC) in natural marine environments – ennoblement and sulfate reduction that leads to sulfide derivitization. Both are global phenomena and both depend on the presence of oxygen for aggressive attack. Marine biofilms cause a noble shift, or ennoblement, in corrosion potential (E_{corr}) for most passive alloys. E_{corr} ennoblement increases the probability for pitting and crevice corrosion initiation and propagation for those passive alloys where E_{corr} is within a few hundred millivolts of the pitting potential (E_{pit}) (e.g. 304L and 316L stainless steels). Numerous researchers have shown that increased cathodic oxygen reduction reaction (ORR) rates accompany ennoblement of E_{corr}, but do not agree on a universal mechanism for acceleration of ORR by biofilms. The role of oxygen in accelerating marine sulfide influenced corrosion has not been precisely defined. Past experiments have demonstrated that dissolved oxygen (DO) in stagnant natural seawater (8 ppm) exposed to corroding carbon steel will be depleted to the detection limits of an electrochemical probe (100 ppb) within 48 h due to aerobic microbial respiration and corrosion reactions. Furthermore, most solid surfaces in contact with seawater are anaerobic because the rate of microbial respiration within a biofilm is greater than the rate of oxygen diffusion. Even in an oxygenated bulk environment, sulfate-reducing bacteria (SRB) dominate anaerobic niches in marine biofilms and produce aqueous sulfides that can derivitize some metals and alloys (e.g., carbon steel and copper-based alloys). In the absence of oxygen, corrosion will slow or cease as bare metal, surface oxides and metal ions are derivatized forming protective surface metal sulfides. Whereas in the presence of oxygen, the protective surface-bound sulfides are oxidized thus allowing more corrosion reactions can take place. In addition, introduction of oxygen (e.g., flow after stagnation) dramatically increases instantaneous corrosion rates owing to metal sulfides being more efficient oxygen reduction cathodes compared to metal oxides. The end result is deeper metal penetration when compared to strictly anaerobic environments. More recent experiments have demonstrated that even transient DO in the bulk medium can influence the microflora and corrosion rates of carbon steel. Using optical DO probes (detection limits 4 ppb) bulk concentrations of DO in the bulk medium are being correlated with corrosion rates and pit depths in carbon steel. Persistence of aerobic bacteria at ppb DO is being followed.

2:40pm **MB+BI-ThA3 3D-Tracking of Biofouling Microorganisms with Digital In-Line Holographic Microscopy**, ***S.M. Stuppy***, University of Heidelberg, Germany, *A. Rosenhahn, T. Schwartz,* Karlsruhe Institute of Technology, Germany, *T. Ederth,* Linköping University, Sweden, *J.A. Callow, M.E. Callow,* University of Birmingham, UK, *B. Liedberg,* Linköping University, Sweden, *G.W. Swain,* Florida Institute of Technology, *M.H. Grunze*, Karlsruhe Institute of Technology, Germany

Digital in-line holographic microscopy, based on Gabor´s initial idea of a lensless microscope[1], is an imaging technique which allows to track microorganisms in three dimensions. A so-called "source wave" interferes with the wave scattered off the swimming objects and forms an interference pattern (Hologram) on the detector which contains three-dimensional information of the objects investigated. To obtain real space information from the Hologram, a reconstruction algorithm is applied[2]. The reconstructed data provides 3D trajectories of single spores with a 10 Hz time resolution and thus allows a qualitative and quantitative analysis of swimming behavior and settlement kinetics of microorganisms such as marine biofoulers or pathogen bacteria down to a lenght of 1-2 µm.

In our recent work the swimming and settlement behavior of *Ulva linza* zoospores as a common motile biofouling organism was investigated in the vicinity of surfaces with different chemistry[3-5]. We analyzed the effect of fast and abnormal settlement of *Ulva* spores on a charged Arginin containing oligopeptide surface[6] by digital holography to study the exploration behavior and kinetics of the colonization of the surfaces. As step towards application of holography at ocean test sites in the field, we constructed a compact holographic setup and tested it at the FIT test site and studied the swimming behavior of small marine organisms in their native environment.

We also applied holography to study motile biofilm forming bacteria. Using a large CMOS sensor, we were able to resolve and track rod shaped bacteria with a length of 2 µm, namely the pathogen *Pseudomonas aeruginosa*. We will show the first three-dimensional trajectories for a free swimming *Pseudomonas aeruginosa*.

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3:00pm **MB+BI-ThA4 A Multidisciplinary Approach to Tackling Microbiologically Influenced Corrosion**, ***S.A. Wade***, *P.R. Stoddart, E. Palombo, M.M. Hlaing, M.A. Javed, D. Marić, D. Eldridge, S.L. McArthur*, Swinburne University of Technology, Australia

Microbiologically influenced corrosion (MIC) can lead to localized material degradation rates that are orders of magnitude higher than would normally be expected from standard, abiotic corrosion. This can lead to the premature failure of a wide range of important structures that can not only be costly to repair, but in some cases can have fatal consequences.

Studies of MIC require expertise from a wide range of fields such as material science, microbiology, chemistry and engineering. However, much of the past work that has been undertaken on MIC has been performed with a discipline-specific focus. This is somewhat understandable in a historical research context and may help to explain some of the observed discrepancies between MIC studies undertaken in the laboratory and field observations. In order to overcome some of these issues and develop solutions to the problems caused by MIC a multidisciplinary approach is required.

We have assembled a multidisciplinary team to investigate two specific aspects of MIC, namely the composition of bacterial consortia implicated in MIC and the associated physicochemical processes that drive MIC.

With respect to bacterial identification work is being carried out using a variety of techniques, including the relatively novel application of MALDI-TOF and Raman spectroscopy to MIC. The latter technique is particularly attractive as it potentially allows single bacteria to be identified at different stages of their life cycle, as well as in biofilm. Initial work in this area has required the development of data analysis techniques in order to remove background fluorescence signals in a consistent manner. MALDI-TOF potentially allows rapid routine identification from large numbers of samples. Initial results obtained with this technique will be presented.

The second area of interest includes work undertaken to look at how changes in field conditions can affect the likelihood of MIC. Metal coupon corrosion tests using seawater samples obtained from different field locations have been performed. A range of metallurgical, chemical and microbiological measurements were made to investigate differences observed for samples tested in two different seawater solutions and also for replicate samples tested using seawater from the same location.

Although progress remains challenging, the multidisciplinary approach reported here is showing great promise, with chemists, metallurgists and physical scientists working closely with microbiologists to understand the full complexity of the underlying biological processes.

3:40pm **MB+BI-ThA6 Bioinspired Surfaces with Dynamic Topography for Active Control of Biofouling**, ***X.H. Zhao***, *G.P. Lopez, D. Rittschof*, Duke University

Biofouling of ship hulls and propellers increases drag and power usage and decreases fuel efficiency. Biofouling costs the US Navy alone approximately one billion dollars per year, and the decreases in fuel efficiency further increase green-house gas emissions. Traditional antifouling coatings, relying primarily on biocidal organics and metals, have negative environmental impacts, while newer polymer-based coatings are easily damaged and ineffective in long-term applications.

On the other hand, nature has created an enormous number of biological surfaces that can effectively clean themselves via active deformation and motion. For example, tiny hairs called cilia on the surfaces of respiratory tracts constantly move back and forth, pushing inhaled foreign particles out of our lungs. The ciliary cleaning has also been used by molluscs, corals and many other marine organisms for active antifouling.

Inspired by active biological surfaces found in nature, we have developed a novel active-antifouling technology by harnessing dynamic deformation of polymer coatings in response to external stimuli. We discover that the surfaces of silicone-based coatings can be significantly deformed by applying a direct-current voltage across the coatings. The deformation is on-demand, dynamically switching the coating surfaces between patterned and flat states as the applied voltage is on and off. The on-demand deformation can actively and effectively detach various biofouling organisms such as bacterial films and barnacles adhered on the polymer coatings. The new technology can be readily integrated with existing or newly-developed polymer coatings, combining the advantages of various state-of-the-art antifouling technologies. This new active-antifouling system is environmentally friendly, autonomous, highly effective, and potentially durable over long-term applications. Next, we will further discuss the fundamental effect of active surface deformation on marine organism-surface interactions. A new theory for biofouling detachment caused by substrate deformation, instead of external forces, will be presented.

4:00pm **MB+BI-ThA7 Seasonal Study of Cathodic Current and Elucidation of Oxygen Reduction Enhancement Mechanism in Marine Biofilms**, ***M.J. Strom***, Naval Research Laboratory, *S.C. Dexter*, University of Delaware

The ability of a biofilm to influence the corrosion rates through the enhancement of cathodic currents is well known but what mechanisms cause this enhancement and how sustainable is it during seasonal variation? Enhancement of the oxygen reduction reaction has been shown to occur in Delaware Bay waters. Historically, enhancement of the oxygen reduction reaction by biofilms has been attributed to the presence of catalase in biofilms. However, recent work has indicated that manganese oxides may also provide a means for oxygen reduction enhancement in. The following investigation looks at the effect of seasonal variation of the sustainability of oxygen reduction enhancement and distinguishes between manganese and catalase based mechanisms

The following work used sacrificial anodes to provide a long-term cathodic current to biofilm-coated cathodes in Delaware Bay waters, in order to monitor seasonal variation of biofilm-coated cathodes under varying polarization intensities over a year. Manganese and catalase based oxygen reduction enhancement mechanisms were evaluated through the addition of glutaraldehyde or formaldoxime (FAD) treatments to the bulk solution of immersed galvanic couples.

Varying the polarization intensities of 6XN cathodes in a galvanic couple with a sacrificial anode has provided further evidence that the sustainable cathodic current enhancement found by biofilms of Delaware Bay is a result of oxygen reduction enhancement. Glutaraldehyde treatment experiments indicate that a catalase mechanism of oxygen reduction enhancement is not likely in at this location. FAD treatment experiments support the hypothesis that manganese oxides are the dominant catalysts in oxygen reduction enhancement in these waters. Seasonal studies of cathodic current enhancement show that cathodic current enhancement in Delaware Bay is seasonally dependent, with higher cathodic currents in the late spring to early fall. It is suggested that this variation is the result of the biological activity of the surrounding sediments providing a manganese resource into the water column during the warmer seasons.

4:20pm **MB+BI-ThA8 Tailoring Anode and Cathode Biofilms for Higher Current Production in Bioelectrochemical Systems**, ***J. Regan***, Penn State University **INVITED**

Bioelectrochemical systems (BESs) exploit the ability of some microbes to reduce an anode (exoelectrogenesis) or oxidize a cathode (exoelectrotrophy) for the generation of electrical current coupled with some biotransformation. There has been a lot of research in the past decade on improving the performance of BESs, primarily by addressing system features that allow reduced internal resistance. These design advancements have led to more than a six order of magnitude increase in power densities in that short time period. Moreover, a growing number of potential BES applications are being developed, including electricity production from wastes and sediments in microbial fuel cells for remote or centralized power, the production of fuels such as hydrogen and methane in microbial electrolysis cells, the recovery of value-added chemical products such as caustic and hydrogen peroxide, water desalination in microbial desalination cells, and microbial electrosynthesis for the production of organic products. Some design and operation parameters can have significant effects on anode and cathode biofilm architecture, composition, and functionality. For a given system configuration (e.g., electrode material, electrode spacing, membrane), there are only a few parameters that can be manipulated during operation. One of these operational variables is the external load or the applied potential in a potentiostatically operated system, which can significantly affect the microbial ecology of BESs as it influences the availability of the anode to serve as an electron acceptor for exoelectrogens and thereby controls the cooperation and competition among various community members in mixed-culture systems. This directly translates into performance effects, not only with respect to the time required to achieve a desired electron donor removal efficiency, but also with electron losses to competing metabolisms such as methanogenesis and aerobic respiration in an air-cathode system. This presentation will cover the mechanics of BESs, including some of the emerging designs and applications, as well as some of the parameters than can be manipulated to include microbial function, density, and productivity.

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