Tuesday Afternoon, October 21, 2008

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+PS+AS+BI+SS-TuA

Plasma-deposited Polymer and Organic Surfaces in Biological Applications
Moderator: E.R. Fisher, Colorado State University

1:40pm **BO+PS+AS+BI+SS-TuA1 High Throughput Surface Chemical Analysis of Polymer Microarrays: Wettability, Protein Adsorption and Cell Response Correlations**, *M. Taylor, A.J. Urquhart,* The University of Nottingham, UK, *Y. Mei, D.G. Anderson, R. Langer,* MIT, *M.C. Davies,* ***M.R. Alexander***, The University of Nottingham, UK **INVITED**

In the search for new and improved biomaterials, combinatorial material discovery approaches are increasingly being explored. A significant development in the production of polymer libraries by parallel synthesis was the move from preparation of macroscopic samples,[1] to on-slide polymerisation as microarrays in nano-litre volumes.[2] Such microarray material libraries may readily be interrogated by automated surface analysis equipment. Recently, high throughput surface analysis of a library of 576 different acrylate copolymers in triplicate on one slide using water contact angle (WCA), XPS and ToF SIMS highlighted the difference in the bulk and surface composition of the polymer spots, and consequently the need for surface analysis data when determining structure-property relationships.[3] The complexity of SIMS data, multiplied by the number of different samples necessitates the use of multivariate analytical approaches. Using partial least squares (PLS) analysis, relationships between SIMS fragments and WCA have led to identification of moieties controlling wettability across the wide range of copolymers synthesised on one microarray.[4] Comparison of human embryonic stem cell number on the spots with SIMS spectra have identified further SIMS fragments that correlate with high or low cell-polymer affinity. Protein adsorption measurements have been undertaken in an attempt to rationalise the cell adhesion data.[5] The correlations identified, and the information on the relationship between the surface structure and cell response or wettability will be discussed in this exploration of the high throughput approach.

[1] Brocchini S et al. Structure-property correlations in a combinatorial library of degradable biomaterials. Journal of Biomedical Materials Research 1998 42 66.

[2] Anderson DG, et al. Nanoliter-scale synthesis of arrayed biomaterials and application to human embryonic stem cells. Nature Biotechnology 2004 22 863.

[3] Urquhart AJ, et al. High throughput surface characterisation of a combinatorial material library. Adv Mats 2007 19 2486.

[4] Urquhart AJ et al. TOF-SIMS analysis of a 576 micropatterned copolymer array to reveal surface moieties that control wettability. Anal Chem 2008 80 135.

[5] Taylor M et al. A Methodology for Investigating Protein Adhesion and Adsorption to Microarrayed Combinatorial Polymers. Rapid Macromol Comm 2008 (in press).

2:20pm **BO+PS+AS+BI+SS-TuA3 Plasma Medicine**, ***A. Fridman***, Drexel University **INVITED**

Novel engineering and science approaches sustaining human health, such as for example radiation biology and laser medicine, represent a significant segment of technological developments around the world. Recent breakthrough discoveries of the highly energetic but non-damaging direct treatment of living tissues with non-thermal plasma enable to create new branch of the engineering medicine, PLASMA MEDICINE, which creates qualitatively new possibilities of healing, treating of previously untreated diseases, deactivation of dangerous pathogenic organisms, development of new direct methods of medical diagnostics. New types of non-thermal atmospheric plasma discharges are able to operate directly contacting human body and other living tissues, which significantly increase effectiveness of the tissue sterilization, treatment of wounds, skin and other diseases, as well as direct medical diagnostics. Obviously success of the plasma medicine depends on deep fundamental understanding of physics, chemistry and biology of the non-thermal plasma interaction with living tissues, and engineering of the relevant non-thermal plasma discharges, which is to be discussed in the presentation. Recent achievements in plasma biotechnology also address many aspects of the challenging problem of deactivation of viruses and bacteria that cannot be disinfected by traditional methods. Disinfecting large volumes of air in buildings and hospitals economically is now possible with room-temperature atmospheric pressure plasma. Similarly, atmospheric plasma technology can be employed to sterilize medical equipment, clothing, and building walls; to disinfect living tissue without side effects, and to disinfect and preserve food and water without damage. In addition, plasma technology can also be used to create innovative tools for sensing, detection and identification of dangerous pathogenic organisms as well as to characterize success of the cleansing processes. Essential advantage of the plasma biotechnology is its potential for universal availability, due to the technology's exclusive reliance on electrical power. It avoids many logistical difficulties associated with delivery, storage and disposal that typically hinder chemical and pharmaceutical approaches to sustainable health. Plasma technology can also be easily scaled from point-of-use devices to centrally operated plants capable of cleaning massive quantities of material. The key element of recent plasma technology developments is its use as a catalyst of many natural biological processes. As such, plasma can provide highly energy efficient treatment of biological materials, which is also to be discussed in the presentation.

3:00pm **BO+PS+AS+BI+SS-TuA5 Plasma Polymer Patterning of PDMS for Microfluidic Application**, ***S. Forster***, *A.G. Pereira-Medrano, M. Salim, P.C. Wright, S.L. McArthur*, University of Sheffield, UK

Microfluidic systems are becoming increasingly important for a wide range of bioengineering applications including proteomics and protein separations. Polydimethylsiloxane (PDMS) has proved to be the most popular material for microfluidic device production in the laboratory due to its many advantages over traditional materials. However, PDMS has some fundamental problems, namely a lack of functionality present at the surface, high protein fouling and inability to retain stable surface modification due to its motile hydrophobic monomer. These factors can lead to the loss of specificity and sensitivity in many bioassays. Plasma polymerisation is a method of depositing a uniform polymeric coating onto a surface, while retaining the desired functionality of the monomer. Hence, plasma polymerisation presents a versatile approach for surface modification and patterning of device channels. The wide range of monomers available for plasma polymerisation makes this approach even more suitable for use in systems where multiple surface properties within a single device are required. The aim of this work was firstly to investigate methods to produce stable plasma polymer patterns on PDMS. The coatings chosen include acrylic acid and maleic anhydride for their functional groups and tetraglyme to reduce non-specific protein adsorption. Patterning using photolithographic techniques and subsequent specific biomolecule immobilisation was achieved. Surface characterization using XPS and ToF-SIMS was used to ensure the spatial, chemical and biomolecule resolution of the device surfaces produced. This ability to combine microfluidics with spatially defined reactive regions on a 'non-fouling' background was then used in a number of applications to show the diversity and efficiency of the devices. Protein digestion by immobilized trypsin using single flow-through experiments in PDMS devices was improved using plasma polymer functionalized channels. The results achieved using mass spectrometry showed an increase in speed and sensitivity of the digestion as well as superior device reliability. Finally, plasma functionalized channels were used to investigate the effect of ampholyte adsorption onto device walls in isoelectric focusing (IEF). By coating channels with a tetraglyme plasma polymer an increase in sensitivity and reproducibility of IEF measurement was achieved. This technique can also increase the 'lifetime' of the device by ensuring channel properties were unchanged.

4:00pm **BO+PS+AS+BI+SS-TuA8 Plasma Etching for Selective Removal of PMMA from nm-scale PS/PMMA Block Copolymers for Lithographic Applications**, ***A.E. Wendt***, *Y.H. Ting, C.C. Liu, X. Liu, H.Q. Jiang, F.J. Himpsel,* University of Wisconsin-Madison, *P.F. Nealey*, University of Wisconsin, Madison **INVITED**

Diblock copolymers films, in which polymer components segregate into nano-scale domains, have been shown to have tremendous potential in fabrication of nm-scale surface topographies. Applications range from microelectronics fabrication to the study of how topography affects the growth and behavior of living cells or microorganisms. Use of block copolymers as a template for pattern transfer requires selective removal of one polymer component, and has motivated our study of plasma etching of polystyrene (PS) and polymethyl-methacrylate (PMMA), the two components of the PS-PMMA diblock copolymer. To better understand the mechanisms of the etch process for these materials, we have surveyed the effects of etch gas mixture and ion bombardment energy (taking advantage of our capability to produce a narrow ion energy distribution at the substrate), in combination with chemical analysis of the resulting etched surfaces. Of particular interest are the mechanisms of surface roughening, which shows a complex dependence on plasma process conditions that is not easily explained. A review of the literature on factors contributing to surface roughness, such as intrinsic inhomogeneity in the film, local deposition/micro-masking, shadowing effects and redeposition will be presented. We ultimately propose a mechanism for roughening of PS that involves micro-masking by inhomogeneous modification of surface chemical composition (rather than deposition) in oxygen-containing plasmas. Support from the UW NSF MRSEC for Nanostructured Materials is gratefully acknowledged.

4:40pm **BO+PS+AS+BI+SS-TuA10 Correlation of Macroscopic Surface Qualities of Poly-Parylene with Plasma-Specific Parameters**, ***G. Franz***, *F. Rauter, M. Häge*, University of Applied Sciences, Germany

In the course of our research how deposition conditions teleologically influence the morphology and various physical properties of the surface of various derivates of parylene, we followed the Yasuda approach to correlate the deposition rate of polymeric films with external parameters (flow rate and power) to define three different regimes of growth.[1,2] Since external parameters, especially the pressure, influence the polymerization in an opposite manner (rising the pressure causes an increase in the collision rate, but a decrease in electron temperature) we studied the deposition of parylene vapors with and without pulsed microwave plasmas to correlate outcome parameters such as surface energy, roughness, and deposition rate with respect to plasma density and electron temperature (Langmuir and OES) by varying the molar fraction of the monomeric species, diluted by the noble gas argon, the total pressure and the power. For this end, we determined the vapor pressure of the dimer and the chemical equilibrium between the monomer and the dimer by varying the evaporation temperature and the cracking temperature, resp., and cross-checked this equilibrium by mass spectrometry. This method has been extended to explain the onset of volume polymerization which becomes manifest by slight tarnishing of the polymer. Following Yasuda, this happens when a certain ratio of number density of the monomeric species to plasma density is exceeded. After having established stable process windows, two further tracks have been followed, namely copolymerization with CF_4 (volume polymerization) and hydrophilic functionalization. Following Gogolides, the surface roughness has been correlated to contact angle measurements.[3] The super-hydrophobic character is mainly due to surface roughening (nanotexturing) in the case of normal CVD. However, plasma treatment leads to super-hydrophobic character also for smooth surfaces. Subsequent treatment with O_2 generates long-term stable hydrophilic surfaces. To calibrate the effect of momentum transfer and to separate the chemical effect of etching, this has been compared with Ar etching.

[1] H.K. Yasuda, and Q.S. Yu; J. Vac. Sci. Technol. A 19, 773 (2001)
[2] Q. Yu, C.E. Moffitt, D.M. Wieliczka, and H. Yasuda; J. Vac. Sci. Technol. A 19, 2163 (2001)
[3] A.D. Tserepi, M.-E. Vlachopoulou, and E. Gogolides; Nanotechnology 17, 3977 (2006).

5:00pm **BO+PS+AS+BI+SS-TuA11 Plasma Processing of Nanostructured Polymeric Surfaces for the Development of Immunosensors**, *A. Valsesia*, ***P. Colpo***, *I. Mannelli, G. Ceccone, F. Rossi*, European Commission Joint Research Centre, Italy

Immunosensors play a very important role for the development of Point-of-Care analysis thanks to their rapid and sensitive detection capabilities.[1] Among others, the control of the interface between the transducer and the biological probes is a crucial issue since the bio-interface is the essential element that guaranty the bioactivity of the immobilized biological probes.[2] The control of the bio-interface is typically addressed by functionalizing the surface with special chemical groups. Besides, new nanobiotechnology-based tools have led to more sophisticated approaches that use for instance nanostructured surfaces. Benefits have been already shown in terms of the improvement of immunoreaction efficiency.[3] In this work we propose a new method for fabricating nanostrucured surfaces combining the use of colloidal masks with different plasma processes. In this method, Plasma Polymerization Processes are able to produce pinhole-free functional layers with different properties. The choice of the precursor together with the appropriate plasma processing parameter ensures the production of stable functional layers which can be used for the production of the chemically contrasted nanopatterns. Also the deposition of the colloidal mask in a controlled way is essential: for example, mass sensitive detectors (like Quartz Crystal Microbalance, QCM) require the use of very large areas in order to obtain measurable signals. Also plasma etching plays a very important role: it is important to choose the suitable processing parameters enabling the fabrication of nanostructured surface which are not limited in the patterning geometry and resolution. After the optimization of the nanofabrication process, the surfaces of immunosensors have been nanostructured. In particular we transferred the nanostructures on the crystals of QCM for on-line monitoring of the protein adhesion. The nanostructures accelerate the kinetics of absorption and increase the density of absorbed molecules, resulting in higher bioactivity of the immobilized proteins and consequently in an improvement of the immunosensing performances.

[1] K. R. Rogers, Applied Biochemistry and Biotechnology - Part B Molecular Biotechnology 2000, 14, 109-129.
[2] B. Kasemo, Current Opinion in Solid State and Materials Science 1998, 3, 451-459.
[3] A. Valsesia, P. Colpo, T. Meziani, P. Lisboa, M. Lejeune, and F. Rossi, Langmuir 2006, 22, 1763-1767.

5:20pm **BO+PS+AS+BI+SS-TuA12 Use of Multivariate Analysis Techniques to Predict Cellular Response to Plasma Polymerized pNIPAM**, ***J.E. Fulghum***, *K. Artyushkova, A. Lucero, H.E. Canavan*, University of New Mexico

The primary objective of this work is to investigate the correlate structural properties of a thermoresponsive polymer, poly(N-isopropyl acrylamide) (pNIPAM), with its ability to reversibly adhere cells. PNIPAM undergoes a sharp property change in response to a moderate thermal stimulus at physiological temperatures (~32 °C). This behavior has generated great interest in the biomaterials community, and pNIPAM is being investigated as a "smart" release coating to harvest intact cell monolayers. Many techniques are used to deposit pNIPAM, including electron beam irradiation and solution deposition (e.g., silanes and self-assembled monomers). Recently, we constructed a radio frequence (rf) plasma reactor for plasma polymerization of NIPAM (ppNIPAM) from the vapor phase based on a previous design. Plasma polymerization is a sterile, solvent-free, and compatible with surfaces of any geometry or chemistry. These factors make plasma polymerization extremely useful for cell and tissue culture, which often rely on plastic tissue culture plates. Due to the inherently energetic conditions of the plasma, parameters such as maximum rf wattage, location/position of the samples in the chamber, and monomer flow have on the resulting films. In this work, pNIPAM films resulting from those varying conditions are characterized using X-ray photoelectron spectroscopy (XPS) for film composition, interferometry for film thickness, contact angles for thermoresponse, and cell detachment for cell releasing properties. Using multivariate analysis, the structural information of the films obtained at various polymerization conditions will be correlated with their thermoresponsive and cell-releasing behavior. In this way, we will predict the conditions that will optimize film composition for bioengineering applications.

Biomaterial Interfaces
Room: Hall D - Session BI-TuP

Biomaterials Interfaces Poster Session with Focus on Cells and Proteins at Interfaces

BI-TuP1 Human Serum Albumin Adsorption to Expanded Polytetrafluoroethylene, ***E.S. Leibner***, *N. Barnthip, W. Chen, C.R. Baumrucker, J.V. Badding,* The Pennsylvania State University, *M.V. Pishko,* Texas A&M University, *E.A. Vogler*, The Pennsylvania State University

Analytical protocol greatly influences measurement of human-serum albumin (HSA) adsorption to commercial expanded polytetrafluororethylene (ePTFE) exhibiting superhydrophobic wetting properties (water contact angles in excess of 150°). Degassing of buffer solutions and evacuation of ePTFE adsorbent to remove trapped air immediately prior to contact with protein solutions are shown to be essential steps that assure reproducible measurement of HSA adsorption. Results obtained with ePTFE as a superhydrophobic test material suggest that vacuum degassing should be generally applied in the measurement of protein adsorption to any surface exhibiting superhydrophobicity. Solution depletion quantified using radiometry (I-125 labeled HSA) or electrophoresis (unlabeled HSA) yield different measures of HSA adsorption, with nearly seven-fold higher surface concentrations of unlabeled HSA measured by the electrophoresis method. This outcome is attributed to the influence of the radiolabel on HSA hydrophilicity which decreases radiolabeled-HSA affinity for a hydrophobic adsorbent in comparison to unlabeled HSA. These results indicate that radiometry underestimates the actual amount of protein adsorbed to a particular material. Removal of radiolabeled HSA adsorbed to ePTFE by 3X serial buffer rinses also shows that the remaining "bound fraction" was about seven-fold lower than the amount measured by radiometric depletion. This observation implies that measurement of protein bound after surface rinsing significantly underestimates the actual amount of protein concentrated by adsorption into the surface region of a protein-contacting material.

BI-TuP2 The Role of Surface Chemistry in poly-L-lysine Mediated Alginate Adsorption, ***K.T. Queeney***, *J.E. Brown, E.K. Davis, C. Franqui*, Smith College

Adsorption of polysaccharides to solid substrates, an essential component of biofilm formation, is generally protein-mediated. Lysine-rich proteins, in particular, are known to have significant adhesive properties in these systems. This work uses poly-L-lysine (PLL) as a model protein to explore the role of the underlying substrate in protein-mediated adsorption of alginate, a negatively-charged polysaccharide. We have prepared films of varying PLL coverage on two types of surfaces: hydrophilic, negatively-charged silica and a hydrophobic, electrically neutral alkylsilane monolayer. PLL coverage on the hydrophilic surface is controlled by varying the ionic strength of the adsorption solution, while PLL coverage on the hydrophobic surface is controlled by varying the molecular weight of the PLL. By a combination of techniques--primarily ellipsometry, dynamic contact angle goniometry and atomic force microscopy--we demonstrate that not only the film morphology of the PLL but also its effect on subsequent alginate adsorption is highly sensitive to the surface chemistry of the underlying substrate. For example, PLL films on silica are more discontinuous at low and high ionic strength, and alginate adsorption is highly influenced by this discontinuity, which allows for repulsive electrostatic interactions between the surface and the alginate. In contrast, while there is an increase in PLL film discontinuity as a function of increasing PLL molecular weight, alginate adsorption appears largely insensitive to these changes in PLL film morphology. Through quantitative analysis of the advancing contact angles on both these (chemically heterogeneous) surfaces we demonstrate unequivocally that the PLL/solution interface is highly dependent on both substrate surface chemistry and PLL adsorption conditions.

BI-TuP3 Time of Flight Secondary Ion Mass Spectrometry Characterization of the Surface Polysaccharides of Group B Streptococcus, *T. Nguyen,* Oregon State University, ***J.R. Hull***, *D.G. Castner*, University of Washington NESAC/BIO

Group B Streptococcus (GBS) is a leading cause of sepsis and meningitis in neonates and immunocompromised adults in western countries. The surface of GBS is well characterized by standard microbiological techniques and therefore makes a good test system for analyzing bacteria using Time of Flight Secondary Ion Mass Spectrometry. GBS is layered with a capsule composed of five distinct polysaccharides containing glucose, galactose, N-acetylneuraminic acid, rhamnose, and N-acetylglucosamine. The capsule makes up 10 to 30% of the dry weight of the microorganism and is only present on the surface. In this work, the five monosaccharides, pure capsule from type III GBS, and UV killed GBS strain COH1 and acapsular GBS strain COH1-13 were investigated. It was observed that the pure monosaccharide fragmentation patterns followed $C_xH_{2x}O_x^+$, and that the largest fragment observed of the monosaccharides was with the loss of H_2O, OH^- or H_3O^+. The presence of sodium, magnesium, and calcium in the purified samples made direct comparison with the pure monosaccharides difficult due to cationization effects. Spectra from clusters of GBS and single organisms were acquired using the high mass resolution imaging mode and constructing a spectrum from a region of interest. The biggest differences between COH1 and COH13 were seen in the high mass region of the spectra.

BI-TuP4 Hydrogels with KGF, ***J.A. Appawu***, *J.A. Gardella*, University at Buffalo: The State University of New York

XPS and TOF-SIMS are techniques that can be used to quantify the uptake and release of proteins from polymers. Hydrogels are cross-linked hydrophilic polymers used in localized delivery of growth factors through pores defined by type and density of cross-links. Therefore uptake and release are diffusion controlled. Keratinocyte growth factor 1(KGF-1) is known to promote re-epithelialization after skin injury and stimulate the proliferation of skin cells. Inadequate amounts of growth factors can result in inefficient healing. In this study, (hydroxyethyl methacrylate) (HEMA) hydrogels 3% and 6% were prepared with varying cross-link densities to answer three key questions:1) What is the optimal concentration of KGF-1 for cell adhesion, 2) Are HEMA hydrogels with specific structural properties viable for cell proliferation, and 3) What is the amount and time course of released KGF-1 present on the surface? Hydrogels were cut into equal areas to determine the amount of KGF-1 protein taken into and released from the hydrogels by fluorescence spectroscopy. XPS was used to confirm the quantity of KGF-1 on the surface and bulk by varying the take-off angle (TOA). The nitrogen atomic concentration was used to track the protein since nitrogen is present only in KGF-1. The amount of KGF-1 was higher in the 3% hydrogel due to a swelling ratio of 58.5% compared to 40.5% for the 6% hydrogel. Cell adhesion experiments have shown that 80-90% of HaCaT cells successfully adhere to the surface of the KGF-1 imbibed hydrogels and fluorescence microscopy proved that the cells were alive. TOF-SIMS has been used in depth profiling to confirm the XPS results.

Mahoney C. M., Yu J., Fahey A., and Gardella J. A. Jr. SIMS Depth Profiling of polymer blends with protein based drugs. Applied Surface Science (2006) 6690-6614. Pierce G.F. et. al. Stimulation of All Epithelial Elements during Skin Regeneration by Keratinocyte Growth Factor. J. Exp. Med. (1994) 179, 831-840. Tsuboi R. et al. Keratinocyte Growth Factor (FGF-7) Stimulates Migration and Plasminogen Activator Activity of Normal Human Keratinocytes. J. Invest. Dermatol. (1993) 101, 49-53. Greenhalgh D. G. The role of growth factors in wound healing. J. Trauma. (1996) 41, 159. Mahoney C. M., Yu J., and Gardella J. A. Jr. Depth Profiling of Poly(L-lactic Acid)/TriBlock Copolymer Blends with Time-of-Flight Secondary Ion Mass Spectrometry. Anal. Chem. 2005 77, 3570-3578.

BI-TuP5 Patterning of pOEGMA Polymer Brushes Using Photolithography and Photomasking for Applications in Protein and Cellular Adhesion Research, *M.S. Johannes, A. Garcia,* ***A. Hucknall***, *A.J. Simnick, R.L. Clark, S. Zauscher, A. Chilkoti*, Duke University

We report the use of bulk microfabrication processes to pattern non-fouling, surface-initiated poly-oligoethylene glycol methacrylate (pOEGMA) polymer brushes. Previous studies have demonstrated the non-fouling capability of pOEGMA surfaces through protein absorption and cell adhesion studies. Here, we demonstrate that the polymer brushes on a glass substrate can be easily patterned using two processes. In the first one, standard photolithography is used to pattern both negative and positive photoresist spin-coated on the pOEGMA layers. The patterned photoresist layers act as masks for the removal of exposed underlying pOEGMA layers by UV-O3 exposure and oxygen plasma ashing. Upon photoresist stripping, patterns with a resolution down to ~400 nm are achieved. In the second approach, TEM grids are directly placed on the pOEGMA layer to block the brushes from direct exposure to various oxidative species offering great simplicity, high-throughput, and low-cost. Successful patterning of non-fouling surfaces at both the micron and nanometer scale will have importance in developing patterned cell monolayers and studying linear motor protein locomotion.

BI-TuP6 Novel Patterned Protein Assay To Measure Differential Extracellular Matrix Protein Affinities for Cellular Attachment and Axonal Outgrowth, ***W.M. Theilacker***, *A.L. Styer, H.P. Bui,* University of Delaware, *D.E. Willis, J.L. Twiss,* Alfred I. DuPont Hospital for Children, *T.P. Beebe, Jr.*, University of Delaware

Cellular preference for extracellular matrix (ECM) proteins was assayed on patterned surfaces presenting two ECM proteins that compete for cell attachment and proliferation. Microcontact printing techniques were used to modify silicon substrates with alternating 40-um-wide stripes of the ECM proteins fibronectin and laminin. The spatial distribution of both proteins on the patterned surfaces was measured by epi-fluorescence and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Attachment and outgrowth of dorsal root ganglia (DRG) neurons and neuron-like pheochromocytoma (PC12) cells on striped substrates were analyzed up to 4 days. At each time point, three patterned samples were fixed and immunostained prior to fluorescence imaging. Images were analyzed for the number of cells attached to each protein region and the number and length of neurite extensions. Results indicate for PC12 cells, an approximately equal number of cells on fibronectin and laminin stripes after 24 hours in cell culture. However, from 48 hours to 96 hours, the number of cells on laminin versus fibronectin continually increased. By 96 hours, 80 percent of the PC12 cells were attached to laminin versus fibronectin. Preliminary results for DRG neurons suggest a similar trend, in addition to the influence of Schwann cells, which are known to influence DRG neurite outgrowth.

BI-TuP7 XPS Analysis of Protein Adsorption on Bioprocessing Materials, ***R.A. Zangmeister***, National Institute of Standards and Technology

Protein therapeutics, a fast-growing category of biotech drugs, is adversely affected by protein aggregation. Aggregation can decrease the safety and efficacy of the therapeutic biologic protein product. Currently, the cause of protein aggregation is not clearly understood. The adsorption of protein therapeutics to bioprocessing materials used in production, storage and delivery may create nucleation sites for further protein aggregation. X-ray photoelectron spectroscopy was used to analyze protein adsorption on bioprocessing materials to screen for those with increased probability of contributing to aggregation of the protein therapeutic. The standard overlayer model and protein labeling were used to estimate the thickness of adsorbed protein layers.

BI-TuP8 Highly Sensitive Probe of Crystalline Sub-Micron Sized Domain Structures in Amorphous Material, ***H.B. de Aguiar***, *S. Roke*, Max-Planck-Instiut fuer Metallforschung, Germany

Mixtures of solid compounds or phases occur in a wide variety of chemical processes. Nucleation, crystallization and separation of phases are generally integrative steps in the production of polymer compounds, pharmaceuticals and in many other chemical processes. Many techniques used for analyzing mixtures of medium and ingredients in-situ rely on the interaction of photons with the mixture.[1] Such a situation occurs in solid/solid dispersions, where two different phases coexist, as in the case of most polymers which are known to consist of crystalline domains embedded in an amorphous phase. For instance, Wide-Angle X-Ray Diffraction (WAXS) and Small-Angle X-Ray Scattering (SAXS) are used together to obtain crystallite structure, size and fraction, being limited only by the level of background signal relative to the signal itself. We developed a new technique to study crystalline domains dispersed in an amorphous phase through nonlinear optical Vibrational Sum-Frequency Generation (VSFG) Scattering.[2] VSFG is a second-order nonlinear optical process, which is forbidden in centrosymmetric media (e.g. liquids, amorphous solids). We show the higher sensitivity of VSFG scattering to microspheres (MS) consisted of crystalline and amorphous phase. We studied the scattering pattern of some chiral polymers, namely Poly(Lactic Acid) (PLA). MS made of P(DL)LA polymer (polymer chains consisting of a random distribution of enantiometers) were probed by X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC) as well. XRD and DSC showed no crystallinity of the PDLLA MS, in agreement with previously published studies. However, VSFG spectra and scattering patterns demonstrate that there is still a finite number of crystallites with maximum extension of 250 nm (radii). This indicates VSFG has an increase in sensitivity that is roughly 2 orders of magnitude more than XRD.[3] This opens up new possibilities in the description of early stages of nucleation and growth phenomena and possible new phases.

[1]S Roke et al. Vibrational Sum Frequency Scattering from a Submicron Suspension. Phys. Rev. Lett. 91, 2003, 258302.

[2]AGF de Beer et al. Molecular and microscopic properties of buried microstructures. Submitted.

[3]HB de Aguiar and S Roke. Sum-Frequency Generation Scattering: a higher sensitivity probe for crystalline properties. In preparation.

BI-TuP9 Effect of Film Fabrication Method on the Protein Fouling Resistance of Mixed Oligo(ethylene glycol) Films, ***J.A. Ruemmele***, *M.S. Golden, R.M. Georgiadis*, Boston University

A major concern in the design of biosensors for studying protein interactions is protein fouling, or non-specific binding, which masks the signal from the binding event of interest. Mixed oligo(ethylene glycol) (OEG) films have become a standard surface coating used to avoid fouling of gold sensor surfaces. Such films comprise a probe coupling OEG (A) and a diluent of protein resistant OEG (B). Two methods exist for the fabrication of such surfaces: co-deposition of A and B, and sequential deposition, where A is inserted into a pre-existing monolayer of B. Though films fabricated by sequential deposition display better fouling resistance, the source of this resistance is unclear. It has been hypothesized that the improved fouling resistance is due to an absence of islanding in the film, however it could simply result from an extremely low A content. In order to identify the affect of the fabrication method, films prepared by both approaches must contain the same amount of A. Since few techniques exist which can accurately measure low amounts of A attached to a surface, the amount of probe which covalently couples to a film was used to evaluate the film's A content. Using this technique, the fabrication conditions for both methods were adjusted to produce films containing the same amount of A. The extent of fibrinogen fouling on these now comparable films was measured with surface plasmon resonance imaging to evaluate if the actual fabrication method affects a film's fouling resistance. Furthermore, electrochemically induced reductive desorption was used to indicate any presence of islanding and to evaluate film stability.

BI-TuP10 Specific versus Non-Specific Protein Adsorption: Effects of Chain Length and Tailgroup in Functionalized Poly(ethylene glycol)-Terminated Self-Assembled Monolayers, *P. Buecker, M. Himmelhaus,* ***R. Dahint***, University of Heidelberg, Germany

In recent years, substantial efforts have been made to develop surface coatings which limit or even suppress non-specific adsorption of proteins. While for many technological applications the surfaces are designed to exclusively repel proteins, an even more complex situation exists in biomedical analysis, where immobilized probe molecules, e.g. antibodies, are used to specifically bind target proteins from solution. Here, the coating must fulfil a two-fold function: (i) effectively suppress non-specific adsorption processes, which may both result in false interpretation of binding events and significantly lower the detection limit of the analytical techniques, and (ii) additionally facilitate the integration of the probe molecules without loss of non-specific protein repulsion. Hereby the question arises, to what extent efficient immobilization of probe molecules and suppression of non-specific interactions can actually be achieved with a single material as the repulsion mechanism inhibiting non-specific adsorption of biomolecules might also compromise the integration of the probes. In a recent study we have shown that COOH-functionalized poly(ethylene glycol) (PEG) alkanethiolate self-assembled monolayers (SAMs) [$HS-(CH_2)_{11}-(OCH_2CH_2)_n-COOH$] with a mean number, n, of 33 EG units suppress non-specific protein adsorption while facilitating covalent coupling of antibodies via the terminal COOH-group.[1] We now synthesized the same type of molecule with various EG chain lengths (n = 13-40) and different tailgroups (-OH, $-NH_2$, and -COOH), and compared both the antigen binding capacity and the protein resistance of the corresponding SAMs by ellipsometry, X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FT-IRRAS), and enzyme-linked immunosorbent assays (ELISA). It is observed that protein repulsion depends on the tailgroup selected and increases with increasing EG chain length. In parallel, however, the maximum amount of probe molecules that can be coupled to the films significantly decreases with enhanced EG content, thus, reducing the antigen binding capacity of the films. The results, therefore, show that for bioanalytical applications the number of EG units has to be properly adjusted in order to obtain an optimum signal-to-noise-ratio. The best performance has been observed for a chain length of about 30 EG moieties.

[1] S. Herrwerth et al., Langmuir 2003, 19, 1880.

BI-TuP11 Quantitative Analysis of Angular Resolved XPS-Measurements: Influence of Inaccuracies in Take-Off and Acceptance Angle, ***C. Van der Marel***, *J.H.M. Snijders, D.D.C.A. Van Oers, E.P. Naburgh*, Philips Research - MiPlaza, The Netherlands

For quantitative analysis of Angular Resolved XPS-measurements the take-off angle of the detected electrons is an important input parameter. A device has been developed that allows measurement of the real take-off angle as a function of the tilt angle of the sample. The acceptance angle of the detector is also determined using this device. The device has been tested extensively in two commercial XPS-instruments (Quantera from ULVAC – PHI); small but significant deviations have been found between real and set values of the take-off angles. To investigate the influence of the acceptance angle and of inaccuracies in the take-off angles several series of samples were

analyzed. The samples consisted of a homogeneous substrate coated with a thin organic layer (e.g. phosphonic SAM-layers on Al2O3, alkyl-thiols on copper). Quantitative analysis of the XPS-results provided values for the layer thickness of the organic layer, for the coverage and for the "real" atomic concentrations in substrate and in the organic layer. In the lecture it will be shown that the use of accurate values of the acceptance and the take-off angles is a prerequisite to obtain consistent results.

BI-TuP12 Improved Osseointegration of a Novel, Hydrophilic Ti Surface: Early Events, *A. Molenberg*, ***S. Berner***, Institut Straumann AG, Switzerland, *F. Schwarz, M. Herten,* Heinrich Heine University, Germany, *M. de Wild, M. Wieland*, Institut Straumann AG, Switzerland

The performance of bone-related implants is strongly connected with the properties of the implant surface. Particularly surface topography and chemistry both influence initial wettability and peri-implant bone apposition of implants. Sandblasted and acid etched (SLA) titanium surfaces are initially hydrophobic due to microstructuring and adsorption of hydrocarbons and carbonates. The purpose of this study was to investigate initial hydrophilicity and to examine tissue reactions to a newly developed chemically modified implant surface called SLActive. Implantation of SLActive and SLA implants was performed bilaterally in dogs. The animals were sacrificed after a healing period of 1, 4, 7 and 14 days, respectively. Peri-implant tissue reactions were assessed in nondecalcified tissue sections using conventional histology (Toluidine blue-TB and Masson Goldner Trichrome stain-MG) and immuno¬histochemistry using monoclonal antibodies to transglutaminase II (TG) (angiogenesis) and osteocalcin (OC) (mineralization). Bone density (BD) and bone to implant contact (BIC) were assessed histomorphometrically. Immunohistochemical staining for TG revealed a direct correlation between angiogenesis and new bone formation, which was clearly identifiable after 7 days by means of increasing BD, BIC and OC values. After 14 days, SLActive surfaces seemed to be surrounded by a firmly attached mature, parallel-fibered woven bone. The study clearly reveals an enhanced bone formation for the hydrophilic SLActive surface and thus a reduced healing time.

BI-TuP13 Solution Deposited poly(N-isopropyl acrylamide) Films Optimized for Mammalian Cell Release, ***J.A. Reed***, *M. Bore, L.K. Ista, G.P. Lopez, H.E. Canavan*, University of New Mexico

Poly(N-isopropyl acrylamide), or pNIPAM, is a smart polymer that is of great interest in the bioengineering community. Above its lower critical solution temperature (LCST), the polymer is relatively hydrophobic, and mammalian cells grown on pNIPAM-grafted surfaces act in a similar fashion as those grown on typical tissue culture polystyrene (TCPS): they proliferate into a confluent sheet. Below the LCST (i.e., room temperature) the polymer physically changes, becoming hydrophilic and swelling. Furthermore, when the temperature of the cell culture is dropped below the LCST of the polymer, the cells will detach and can be harvested for tissue engineering applications. This is in contrast to cells grown on TCPS alone, which will not detach using a temperature drop, instead requiring enzymatic digestion (via trypsin) or mechanical scraping to remove them. In this work, we present a novel, solution-based technique to generate pNIPAM surfaces from pNIPAM and tetraethyl orthosilicate (spNIPAM). The composition of the films (i.e., weight % of pNIPAM) was optimized for reversible cell adhesion by observing the thermoresponse, surface chemistry, and cell release characteristics. Characterization of the surface chemistry of the spNIPAM substrates was done using X-ray photoelectron spectroscopy (XPS), interferometry, and contact angle measurements). Characterization of the cell-releasing behavior of the spNIPAM substrates was determined by observing the ability of surfaces to release confluent bovine aortic endothelial cells (BAECs). From these results, we conclude that the fastest, most reliable release of BAECs occurred on surfaces spin coated with a solution of .35wt% pNIPAM/TEOS.

BI-TuP14 Nanometer-scale Cell Adhesive Patches for the Control of Cellular Functions, ***U.A. Martinez***, *T.C. Gamble, G.P. Lopez, E.L. Dirk*, The University of New Mexico

The control of cellular functions will find many applications in the development of new materials for biomedical applications such as tissue engineering. However, for this to be possible, understanding the cell-material interactions is essential. In this work, interferometric lithography was used to create nanometer-scale patterned substrates. Interferometric lithography is a method for fabricating spatially consistent periodic patterns with the use of the interference of two coherent optical beams. The interfering beams produce a standing wave that can be recorded in a photoresist making equally spaced channels. The substrate is then rotated 90° and exposed again creating photoresist pillars. After exposure, the substrates are coated with a 30 nm layer of gold, using a 3 nm layer of chromium to enhance adhesion. An acetone lift-off procedure removes the photoresist pillars, leaving uncoated patches throughout the gold-coated surface. Self-assembled monolayers are formed on the gold-coated areas using thiols of poly(ethylene glycol) [PEG], a biologically inactive molecule that inhibits protein adsorption. Fibronectin, a protein that enhances cellular adhesion, is adsorbed onto the uncoated regions rendering cell adhesive patches. A double exposure technique has also been developed to obtain a two-fold increase in the pitch while holding the same patch size. For example, a pitch of 300 nm with a 100 nm patch can be increased to a 600 nm pitch while maintaining the same size of the patch. These nanopatterned cell adhesive substrates offer a method to systematically manipulate cellular attachment to further control cellular functions such as spreading, viability and differentiation.

BI-TuP15 Competitive Protein Adsorption to Biomaterials and the Dependence on Protein Concentration, ***M. Holmberg***, *X. Hou*, Technical University of Denmark

Quantitative analysis of protein adsorption to artificial materials is of importance in evaluating the potential of biomaterials. Proteins have a central role in all living organisms and are present in basically all parts of the human body and the first thing to happen when an artificial material is introduced into a human body, or another biological system, is unspecific adsorption of proteins onto the surface of the material. Most studies on blood protein adsorption to polymer surfaces reported in the literature are performed from low concentration (≤1 mg/ml) single protein solutions. However, it is not evident that those results also are valid for protein adsorption from protein mixtures with high protein concentration (≥10 mg/ml). When biomaterials are introduced into a human body, thousands of different proteins, sometimes present in quite high concentrations, will come in contact with the material and there will be competitive protein adsorption on the surface of the material. By labelling proteins with different radioisotopes one can monitor the adsorption of several proteins onto surfaces simultaneously, and with this multi-labelling technique one can study competitive adsorption and use complex solutions such as human serum during adsorption experiments. Albumin and IgG (Immunoglobulin G) adsorption to both unmodified and modified PET (polyethylene terephthalate) surfaces from single protein solutions and human serum solutions has been monitored using radioactive labelling. The PET surfaces are modified through plasma polymerisation using the monomer DEGVE (diethylene glycol vinyl ether), which results in a more hydrophilic and anti-fouling surface than the PET surfaces. Results show that the detected anti-fouling quality of DEGVE surfaces is influenced by the concentration of the protein solution used. Albumin and IgG adsorption from human serum dilutions corresponding to 0.1% human serum shows that the albumin and IgG adsorption is significant lower on the DEGVE surface than on the PET surface, and that this antifouling characteristics of DEGVE surfaces can be stable for at least 24 hours. However, performing the same experiment, including the same rinsing procedure, with ≥10% human serum solutions, the detected albumin and IgG adsorption to DEGVE approaches the adsorption detected on unmodified PET. Thus, evaluation of biomaterials should be performed in an environment similar to the one the material is intended to operate in.

BI-TuP16 Scanning Tunneling Microscopy Studies of Photoactive Yellow Protein Anchored to the Thiol Modified Au(111) Surface, ***I.I. Rzeznicka***, RIKEN, Japan, *G.W.H. Wurpel*, Utrecht University, The Netherlands, *M. Bonn*, FOM Institute for Atomic and Molecular Physics (AMOLF), The Netherlands, *M.A. van der Horst, K. Hellingwerf*, University of Amsterdam, The Netherlands, *S. Matsunaga*, The University of Tokyo, Japan, *T. Yamada*, RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan

Adsorption of proteins on metal surfaces and their interactions present an important technological challenge in the field of biotechnology and construction of biomolecules-based functional devices. The process of protein adsorption is very complex and depends on surface properties, protein structure and its chemical composition. On Au surfaces, covalent bonding to the surface can in principle be easily achieved by utilizing unbound sulfur-containing amino acids resulting in the formation of strong Au-S bond, in analogy to the well known thiol chemistry. We studied adsorption of photoactive yellow protein (PYP) protein on Au(111) surface by scanning tunneling microscopy (STM) in air and in the electrochemical environment. The results show that cysteine-containing mutant of PYP does not adsorb on the bare Au(111) surface. Stable, densely packed protein layers were observed after protein immobilization via amide bond formation onto self-assembled monolayers (SAMs), consisting of 3-mercaptopropanoic acid (3-MPA) and 11-mercaptoudecanoic acid (11-MUA) with the use of carbodiimide and N-hydroxysuccinimide. Layers of PYP prepared in this way show fluorescence activity visualized by fluorescence microscopy, indicating that the protein retains its photoactive function upon adsorption. We will also present our attempts to detect a photocurrent generated by laser illumination of PYP layers.

BI-TuP17 Fabrication of Micro-Templates for the Control of Bacterial Immobilization, ***Y. Miyahara***, *N. Saito, O. Takai*, Nagoya University, Japan

Well-defined micro-patterns of bacteria are significant as a fundamental technique for biosensor arrays utilizing rapid detection of infectious diseases and toxic compounds. Many researchers have studied control methods to fabricate the micro-patterns. However, in these researches, many processes are required for the immobilization and the regioselectivity is not so good. In this study, we aim to fabricate well-defined micro-patterns of bacteria using two types of micro-patterned templates and to elucidate the adhesion behaviors of several bacteria onto the templates from viewpoint of surface topology and chemical properties. Super-hydrophobic/super-hydrophilic and super-hydrophobic/polyethylene glycol (PEG) micro-patterns were fabricated as the templates. In the case of super-hydrophobic/super-hydrophilic patterns, the difference of surface energy in the respective regions differs greatly. The difference could have a great effect on the adhesion of bacterial. In the case of super-hydrophobic/PEG micro-patterns, PEG surface generally avoid the adhesion of bacteria due to volume exclusion effect of PEG based on the structural fluctuation. Super-hydrophobic surface was prepared by microwave plasma enhanced chemical vapor deposition (MPECVD) from trimethylmethoxysilane (TMMOS). Super-hydrophobic/super-hydrophilic micro-patterns were fabricated by irradiating the super-hydrophobic surface with vacuum ultra violet (VUV) light through a stencil mask. In the case of Super-Hydrophobic/PEG micro-patterned surfaces, PEG surfaces were fabricated by reacting COOH groups of methoxypolyethylene glycol propionic acid with NH_2 groups of NH_2-terminated self assembled monolayer in ion-exchanged water. The super-hydrophobic regions were fabricated by MPECVD thorough a stencil mask. Bacteria were cultured on the respective templates in the incubator controlled under the CO_2 concentaration of 5 % at 37 ^{o}C. After culture, bacteria were observed by phase-contrast microscope. The surfaces were characterized by XPS and FT-IR. As a result, in the case of super-hydrophobic/super-hydrophilic micro-patterns, some bacteria (Escherichia coli, Bacillus subtilis) were adhered to only super-hydrophobic regions. But others bacteria (Pseudomonas stutzeri, Pseudomonas aeruginosa) were not separated well. Their results attribute bacterial charge, cell division rate and adhesion time lag between super-hydrophobic regions and super-hydrophilic regions.

BI-TuP18 Kinetic Study on Protein Adsorption on Polyelectrolyte Brush Surface, ***H. Tatematsu***, Nagoya University, Japan, *T. Fujima*, Musashi Institute of Technology, Japan, *N. Saito, O. Takai*, Nagoya University, Japan

Polymer chains grafted in the high density stretch perpendicularly by repulsive interaction. This is a so-called brush. The various functional groups can be also introduced into polymer brush as lateral chains. The 3-dimensional structure was varied by the type of lateral chains. On spherical polyelectrolyte brush (PEB), strong adsorption of protein takes place at low ionic strength whereas less protein is adsorbed at the high ionic strength.[1] In addition, protein structure and character remain via adsorption.[2] These properties can be applied to improvement of biocompatibility and Drug Delivery System (DDS). However, the kinetics of adsorption on normal PEB surface has not been understood well. Thus, in this study, we aimed to investigate the kinetics of protein adsorption on PEB. Polystyrene brush (PSB) surface was fabricated by reacting polystyrene terminated by a trichlorosilane (PS-Cl_3) group with silanol (Si-OH) groups on the silicon wafer. PSB brush was converted to polystyrene sulfonate sodium salt brush (PSSB) by sulfonation and neutralization. In protein adsorption experiment, the solution of Bovine Serum Albumine (BSA) in phosphate buffer saline (PBS) was used. NaCl aqueous solution adjusted to various concentrations was added to the stock solution in order to extract the effect of ionic strength. Protein adsorption was evaluated by Fourier transform infrared spectroscopy (FT-IR) and the evanescent adsorption spectroscopy (EOS). The proteins on the surfaces were observed by atomic force microscope (AFM). Relationship between the amount of adsorption and the ion strength on normal PSSB surface differs from that on spherical PSSB surface in previous reports. This would originate from structural configuration of PEB. Finally, we propose a kinetic model of the adsorption on PSSB based on the variation of adsorption against time and ion strength by FT-IR, EOS and AFM.

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BI-TuP19 Surface Characterization of PEG-like Film Made by Using Ethylene Glycol Precursor and Capacitively Coupled Plasma Chemical Vapor Deposition, ***C. Choi***, *S. Lee, D. Jung*, Sungkyunkwan University, Korea, *D.W. Moon, T.G. Lee*, Korea Research Institute of Standards and Science (KRISS)

Polyethylene-glycol (PEG) is widely used for various biological applications because of its anti-fouling property for protein and cells, and non-toxicity in the human body. Since the PEG thin film should have the properties of reproducibility and adhesiveness on various substrates, in this work, plasma-polymerized ethylene glycol (PPEG) thin film was deposited on a glass surface by using the capacitively coupled plasma chemical vapor deposition (CCP-CVD) method and ethylene glycol as a precursor. The PPEG thin films were characterized by using contact angle measurement, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) along with a principal component analysis (PCA). The PPEG surface was controlled in a reproducible manner as a function of sample bias plasma power and was correlated with the surface chemical composition. Of interest, we found that PPEG thin film surfaces deposited at low plasma power were similar in chemical composition to the PEG polymer surface. In addition, by using the fluorescence detection method, we found that the PPEG surface showed an anti-fouling property of immunoglobulin G protein, which was tagged by fluorescein isothiocyanate. Our results showed that this PEG-like PPEG surface would be useful for protein chip applications.

BI-TuP20 Determination of Standard-State Adsorption Free Energy for Peptide-Surface Interactions by SPR Spectroscopy without Peptide-Peptide Interaction Effects, ***R.A. Latour***, *Y. Wei*, Clemson University

As an approach to gaining fundamental insights into the thermodynamics of protein-surface interactions, we are quantitatively determining the standard state free energy of peptide-surface interactions using a host-guest peptide model in the form of TGTG-X-GTGT, where the T (threonine) and G (glycine) flanking sequences are the host residues and X represents a variable guest residue. Alkanethiol self-assembled monolayers (SAMs) with a broad range of polymer-like functionalities are being used as the adsorbent surfaces. With this experimental model, we are able to determine contributions of individual mid-chain amino acid residues on peptide adsorption behavior. The most common way of determining the standard state free energy of adsorption of a peptide to a surface is by use of the Langmuir equation fitted to an adsorption isotherm. This method, however, has the inherent problem of the influence of peptide-peptide interactions at the interface. These effects can substantially affect the shape of the isotherm, leading to errors in the calculated values of the standard state free energy of adsorption. We have developed a new approach to solve this problem and provide accurate, quantitative measurements of the standard state adsorption free energy using surface plasmon resonance (SPR) spectroscopy based on chemical potential relationships vs. the classical Langmuir equation. In addition, we have also developed a very simple, automated method of accounting for bulk shift effects, which can be problematic when doing SPR adsorption studies. These novel methods will be presented along with results for a series of peptide adsorption systems using these methods.

Biological, Organic, and Soft Materials Focus Topic Room: Hall D - Session BO-TuP

Biological, Organic, and Soft Materials Focus Topic Poster Session

BO-TuP1 Photoluminescence Characterization of Highly-Functional Molecule Doped Polythiophene Films Modified by Donor and Acceptor Molecules, ***H. Kato***, *S. Takemura, H. Kobe, Y. Mori, Y. Matsuoka, K. Shimada, T. Hiramatsu, N. Nanba, K. Matsui*, Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with highly-functional molecules such as copper phthalocyanine (CuPc), fullerene C60, and rhodamine B (RB) were synthesized and characterized by photoluminescence measurements in order to fabricate organic hybrid materials with optical emission properties. The changes in photoluminescent properties of the hybrid polymer materials were investigated in the presence of electric field during the synthesis. The affection to the photoluminescence properties by donor and acceptor molecules such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) were also investigated. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and (Et)4NBF4 as a supporting electrolyte and the polymerization on an indium tin oxide (ITO) was conducted by applying positive voltage to the anode. The molecule doping in the polymer film was performed by electrochemical and diffusion methods. Photoluminescence emission peak was observed at 594 nm in the case of PT doped sample with CuPc by diffusion method. The emission peak was observed at 540 nm shifted to the lower wavelength in the case of electrochemically positive voltage applied sample after CuPc was diffused into the PT. Adding C60 molecules to the CuPc diffused PT sample by the diffusion method made the emission peak shift to the higher

wavelength at 730 nm suggesting the molecular interaction between CuPc and C60 in the photoluminescence emission process because double emission peaks were observed at 590 and 735 nm in the case of single doping of C60. In the case of single doping of C60, successive electrochemical process made the double emission peaks single peak at 580 nm. TTF and TCNQ adding to the hybrid polymer films caused peak shift, peak loss and enhancement. In the case of RB diffused PT sample, photoluminescence peak at 590 nm was observed. Electrochemical process made the photoluminescence peak shift which depended on the applied voltage. Adding TCNQ to the RB diffused PT caused the enhancement of the emission peak. The present work clarified that the photoluminescence emission peak position was varied and controlled by electrochemically applying voltage or adding donor and acceptor molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

BO-TuP2 Structured Polyelectrolyte Surfaces: Tunable Surface Morphology and its Influence on Biofouling, ***X. Cao***, *F. Wode, A. Rosenhahn, M. Grunze,* University of Heidelberg, Germany, *J. Fu, J. Ji, J. Shen,* Zhejiang University, P.R. China, *F. Leisten,* University of Hannover, Germany, *R. Mutton, C. Sheelagh, A. Clare,* University of Newcastle, UK, *M. Pettitt, M. Callow*, University of Birmingham, UK

In the search for new coatings to protect surfaces from biofouling in marine environments the surface morphology is one important variable. In order to study the influence of different structure sizes, bioinspired polyelectrolyte multilayer coatings were applied and their effect on the settlement of Ulva linza zoospores and Barnacle cyprids was studied. The multilayers were constructed by the deposition of oppositely charged polyelectrolytes through layer-by-layer deposition. Hierarchical surface structures with different texture sizes and roughnesses were obtained by adjusting the preparation conditions. Surface characterization was carried out by contact angle measurement, spectral ellipsometry, X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy and confocal microscopy to quantify wetting properties, coverage, chemistry, lateral size and aspect ratio of the topographical features. We discuss how variation of the salt concentration changes resulting morphologies. Settlement of Ulva spores and Barnacle cyprids was significantly affected by texture size and roughness. We compare the effect of topography on biofouling with the surface properties and the contact area for the different organisms. Surface modifications with fluorinated silane and poly(ethylene glycol) (PEG) combine the effects of chemistry and topography. Fluorinated, hydrophobic multilayers exhibited higher settlement than the uncoated polyelectrolyte surfaces for Ulva and reduced settlement for barnacle cyprids, while for PEG coated hydrophilic surfaces the anti-fouling performance was drastically enhanced.

BO-TuP3 Characterization and 3D Numerical Modeling of a UV/Ozone Duplex Sterilizer, ***J.E. Jee***, *W.K. Yang, J.H. Joo*, Kunsan National University, Korea

We investigated sterilization characteristics of UV lights by counting the number of bacteria units with varying sterilization time and distance from the light source. When we irradiated 253.7nm on pens, we used UV transparent quartz plate as a support and put a reflecting plate and UV effect is increased about twice. But even with an Al reflector, multi-layered pens could not be treated properly from UV irradiation only. So, we focused on an idea that UV light of 184.9nm could generate ozone and developed a new sterilizer. Ozone generating lamp could treat more uniformly multi-layered pens with a stirring fan by supplying ozone to shadowed surfaces and keep out the temperature rising. Distribution of UV irradiation intensity and ozone supply were analyzed by a 3D model with varying geometry, position of reflectors and fans and confirmed by a semiconductor UV sensor and ozone analyser. We tried to evaluate the enhancement of a TiO_2 photo-catalytic surface by direct sampling with a differentially pumped QMS.

BO-TuP4 Angle Resolved XPS Studies of Plasma Treated Polymers, *P. Mack, T. Carney,* ***R.G. White***, Thermo Fisher Scientific, UK

Plasma treated polymers are becoming more significant in materials applications. Angle resolved X-ray photoelectron spectroscopy (ARXPS) is a useful tool for the analysis of these types of materials, where the modification takes place at various depths in the surface. Advanced data collection protocols, which make use of the Thermo Scientific's unique parallel angle resolving capability, were employed to minimise sample damage whilst maintaining data quality. Additionally, state-of-the-art software was used to maximise the information extracted from the ARXPS data.

BO-TuP5 Time-of-Flight Secondary Ion Mass Spectrometric (ToF-SIMS) Analysis for the Study of the Tertiary Structure of Polysiloxanes in Monolayer Films, Blends and Copolymers, ***H.K. Moon***, *J.A. Gardella*, University at Buffalo

Time of flight secondary ion mass spectrometry (TOF-SIMS) is a powerful technique that can be used to investigate the conformation at the surface of a polymer film. Since the late 1990's TOF-SIMS studies of polymer tertiary structure have been reported for only a few polymers.[1-4] In this study, poly(methylphenylsiloxane) (PMPhS) is studied as another candidate polymer. The films which have the different conformations were manufactured by using Langmuir technique and solution cast method. For these different films, the difference of the fragment ion clusters in the high mass range of TOF-SIMS spectrum was investigated and additionally, reflection-absorption Fourier transform infrared spectroscopy (RA-FTIR) was used to confirm the result of ToF-SIMS. However, previous ToF-SIMS studies of tertiary structures of the polymers at their surface have been limited to the fundamental Langmuir model system.[1-4] Thus, the tertiary structure of poly(dimethylsiloxane) (PDMS) in a more realistic model will be investigated by using ToF-SIMS. First, the tertiary conformations of PDMS monolayers on a polystyrene (PS) substrate, as determined from high mass fragment intensity ratios[4] are determined. Then, the conformations of PDMS blocks, in a PS-PDMS-PS block copolymer, segregated at the surface of blends of PDMS-PS block copolymer and PS homopolymer are determined.[5] Thus, the PDMS film on the PS substrate can be regarded to the intermediate model between PDMS in the fundamental Langmuir film and PDMS segregated at the surface of a PDMS/PS copolymer or blend film.

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BO-TuP6 Partitioning Fracture Energy of a Molecularly Tailored Interface: Bond Cleavage and Plasticity, ***A. Jain***, *Y. Zhou, S. Nayak, P. Ganesan,* Rensselaer Polytechnic Institute, *M. Lane,* Emory and Henry College, *G. Ramanath*, Rensselaer Polytechnic Institute

Separating the work of adhesion and plastic energy contributions to fracture toughness is essential to understand the mechanisms of interface debonding in thin film stacks and tailoring thin interfaces with desired properties for many applications. Here, we quantitatively separate the two contributions for Cu-silica interfaces modified with a molecular nanolayer by four-point bend testing at controlled environments to reveal the controlling mechanisms of energy dissipation. Recent work has shown that annealing Cu-silica interfaces treated with sub-nm-thick molecular nanolayers (MNLs) of a mercaptan-terminated organosilane MNL can yield manifold increase in toughness due to Cu-S bonding and thermally-activated siloxane (Si-O-Si) bridging. The increased fracture toughness, however, exceeds that of fused silica, indicating the importance of secondary absorbing processes in the Cu layer. Since Si-O-Si bridges are susceptible to hydrolysis, varying the water content provides a facile means for tuning the strength of the Si-O-Si bridges, and hence for isolating the contributions of the work of adhesion and the plastic energy. We measured interface toughness of Cu/MNL/SiO2 structures by four-point-bend testing as a function of water partial pressure pH2O under fixed displacement. In all cases, X-ray photoelectron spectroscopy measurements of the fracture surfaces indicated debonding due to siloxane bridge fissure at the MNL-SiO2 interface. The resultant plots of debond rate, V, vs. debond driving energy, G, show two distinct regimes. At pH2O < 1100 Pa, the plasticity in the Cu layer is the dominant contributor to the fracture toughness, as indicated by a high dG/d(ln pH2O), which captures the relative extents of plastic energy dissipation and work of adhesion. At pH2O > 1100 Pa, dG/d(ln pH2O) decreases by a factor of 3, due to the diminished role of large scale plasticity. Thus, our results indicate that interfacial strengthening has a multiplicative effect on the fracture toughness through a factorial contribution due to plastic energy. This result is supported quantitatively by density functional theory calculations of bond stretching in the MNL and siloxane bond breaking in the presence of water. Further, our calculations indicate water decreases the Si-O-Si bond energy by at least a third of its value in vacuum. Our results are of significance for many applications involving molecularly tailored interfaces exposed to environmental and mechanical stresses.

BO-TuP7 Tracking of Motile Organisms by Digital In-Line Holography, ***S. Weisse***, *M. Heydt, A. Rosenhahn*, University of Heidelberg, Germany, *M. Pettitt, M. Callow, J. Callow*, The University of Birmingham, UK, *N. Heddergott, M. Engstler*, Technical University of Darmstadt, Germany, *M. Grunze*, University of Heidelberg, Germany

Digital in-line holography is based on the original idea of D. Gabor's "new microscopic principle". Using this technique an interference pattern of both the so-called "source wave" and the "object wave" is recorded which contains three dimensional information about the observation volume. Real space information about the objects can be retrieved from these holograms through application of a reconstruction algorithm. One great advantage of a holographic instrument is that focusing can be done subsequently on a computer and three dimensional information about the object of interest can be obtained. Micro-fluidic experiments and tracking algae and bacteria, have shown that moving objects can be followed in three dimensions with remarkable accuracy and high time resolution. We present two applications for this technique: understanding biofouling and following the locomotion of pathogens. The exploration behavior of zoospores of the green algae Ulva is monitored to develop a deeper insight on how biofouling occurs on surfaces. Three surfaces (glass, a fluorinated surface and a PEG2000 surface) with different antifouling performances were investigated. For these three samples full 3D motion patterns were analyzed. In the bulk water, far from the surface, spores exhibit the same motility regardless of the investigated surfaces. In close proximity to the surface motility is significantly different. The interpretation of the exploration data leads to the previously unknown conclusion that these three surfaces are colonized via a different mechanism by zoospores. A second application involves examination of the locomotion of the blood parasite Trypanosoma brucei, the causative agent of African Sleeping sickness. The self-propulsion of Trypanosoma brucei in the bloodstream of a mammalian host is an essential part of its ability to withstand the mammalian immune system. To gain deeper insights into the pathogenesis of this blood parasite, a thermo-controllable flow channel setup was developed to allow the measurement of trypanosome trajectories under physiological conditions. Measurements are carried out in a buffer solution with dextran added to mimic the viscosity of mammalian blood and with and without flow to fully characterize motility. The obtained trajectories at different ambient properties are correlated with known effects in pathogenesis.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+AS+BI+NC-WeM

Organized and Structured Organic Interfaces
Moderator: J.S. Shumaker-Parry, University of Utah

8:00am **BO+AS+BI+NC-WeM1 New Approaches to Chemical Lithography on the Micro- and Nanometer Length Scales**, ***N. Ballav***, *S. Schilp*, Universität Heidelberg, Germany, *T. Winkler, H. Thomas, A. Terfort*, Philipps-Universität Marburg, Germany, *M. Zharnikov*, Universität Heidelberg, Germany

The development of novel approaches for the fabrication of nanostructures and, in particular, chemical and biological patterns is an important technological and scientific challenge. One of the perspective methods applies a modification of chemisorbed monomolecular films - self-assembled monolayers (SAMs), which are well-ordered 2D-assembles of long-chain molecules attached to a suitable substrate. A flexible molecular architecture of the SAM constituents allows us to use a wide range of substrates, whereas the molecular size of these constituents makes SAMs an ideal platform for the fabrication of micro- and nanostructures. We present here two new approaches for the fabrication of chemical patterns with aliphatic SAMs as templates. Both approaches rely upon electron beam or X-ray lithography, but require much lower patterning dose as compared to already available methods as, e.g., Chemical Lithography with aromatic templates. The first technique is based on irradiation-promoted exchange reaction (IPER) between the primary SAM template and potential molecular substituent and can utilize a broad variety of commercially available molecules. The key idea of the second method is irradiation-induced activation of amino tail groups of the primary amino-terminated SAM template. Feasibility of both techniques is demonstrated by the fabrication of complex polymer micro- and nanobrushes in a broad height range and, in the case of the IPER approach, by the preparation of micron-scale gradients of protein adhesion.

8:20am **BO+AS+BI+NC-WeM2 Reversible Activation of a Polyelectrolyte Brush: Responsive Monolayers**, ***R. Steitz***, Hahn-Meitner-Institut Berlin, Germany, *V. Papaefthimiou*, TU Berlin, Germany, *J.U. Günther, C.A. Helm*, University of Greifswald, Germany, *S. Förster*, University of Hamburg, Germany, *G.H. Findenegg*, TU Berlin, Germany

Polyelectrolytes anchored on surfaces are important in various applications and are also a challenging topic for fundamental studies. In this work, a monolayer of the PEE114-b-PSS83 [(poly(ethyl ethylene)114-b-poly(styrene sulfonic acid)83] diblock copolymer was transferred from the air/water interface to a deuterated polystyrene coated silicon (dPS/Si) surface, for evaluation as a tunable polyelectrolyte brush containing system. The grafting density of the polymer film was controlled by changing the lateral pressure during the depositions. X-ray Reflectivity and AFM measurements showed that a homogeneous layer of the block copolymer was formed, whose thickness (maximum 8 nm) increased with increasing grafting density. Neutron reflectivity studies against aqueous solutions revealed a hydrophobic PEE layer attached on the dPS/Si surface, and a carpet/brush polystyrene sulfonate (PSS) double layer in water. The effect of salt concentration on the brush nanostructure was investigated in aqueous solutions containing 0-1 M NaCl. It was found that the brush thickness decreases for salt concentrations above 0.1 M. In addition, reversible activation of the brush by changing the ionic strength of the subphase was demonstrated. These results confirm a potential use as a stimuli-responsive polymer for both fundamental studies and biological applications.

9:20am **BO+AS+BI+NC-WeM5 Phase Stability of 2D and 3D Structures of Oligopyridines on HOPG Studied by Thermal Desorption Spectroscopy and Scanning Tunnelling Microscopy**, ***M. Roos***, *H.E. Hoster, R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen bonded 2D networks on graphite (HOPG) at both the solid/liquid[1,2] and the solid/gas[3,4] interface. As found by STM at both interfaces, these adlayer structures depend on the positions of the N-atoms within the molecules, which can be varied via the synthesis process.[1,2] Complementary to the STM studies, we have performed temperature programmed desorption experiments of two different types of BTP molecules on HOPG. This revealed quantitative insights into phase stabilities of 2D (monolayer) and 3D (multilayer) phases. As to be expected from their large mass (618 amu) and correspondingly large moment of inertia, the translational and rotational degrees of freedom are found to play an important, even dominant role for the stability of more or less densely packed phases. This becomes apparent in strongly differing pre-exponential factors for desorption out of 2D and 3D phases. In agreement with STM observations at 300 K, the most stable phase (i.e., the one with the lowest chemical potential) for both molecules is not a close packed hydrogen bonded one, but a dilute 2D gas with facilitated translation and planar rotation. In this picture, ordered, hydrogen bonded structures observed at room temperature are only stabilized by the strong molecule-substrate interaction that allows enforcing higher coverages that go along with the more densely packed, ordered structures.

[1] C. Meier et al., J Phys Chem B 109 (2005) 21015
[2] C. Meier et al., Angew.Chem.Int.Ed. 47 (2008) 3821
[3] H. E. Hoster et al., Langmuir 23 (2007) 11570
[4] M. Roos et al., Phys. Chem. Chem. Phys. 9 (2007) 5672.

9:40am **BO+AS+BI+NC-WeM6 Dielectric Spectroscopy for Biological Applications**, ***C. Prodan***, *C. Bot*, New Jersey Institute of Technology

Dielectric spectroscopy (DS) is a widely used technique to study the properties of cells, proteins and DNA in a fast, label free and noninvasive way. It measures the complex dielectric permitivities as a function of frequency for the given sample. Cellular membrane potential is on of the most important parameter of a living cell and represents the voltage difference between the inside and outside of a cell. Usual values of the membrane potential are in the range of 100 mV. Across a membrane of 2nm thick, this means electric fields of half million V/cm. Theoretical studies have shown that the membrane potential plays a dominant role on the dielectric permitivity of a cell suspension at low frequencies (0Hz-1kHz). Thus the membrane potential can be obtained from a simple measurement of the cell suspension dispersion curves. This talk presents the application of DS to measure and monitor the membrane potential from the low frequency dispersion curves of living cell suspensions of bacteria and mammalian cells. This technique is tested against the standard techniques for measuring the membrane potential such as patch clamping or voltage sensitive dyes.

10:40am **BO+AS+BI+NC-WeM9 True All-Organic Epitaxy in Fashionable Organic Hetero-Junctions**, ***G. Bussetti***, *C. Goletti, P. Chiaradia*, Università degli Studi di Roma Tor Vergata, Italy, *M. Campione, L. Raimondo, A. Sassella, A. Borghesi*, Università Milano-Bicocca, Italy **INVITED**

The improvement of charge transport performances and the control of related electronic properties (a crucial step in the development of organic electronic devices) are strictly connected to the quality of the organic-organic interface, that up to now has been limited by three main problems: 1) the molecular package in organic crystals is significantly influenced by the sample size. It is a difficult task to grow a large single crystal: the substrates commonly used are often assemblies of smaller crystals with different orientations; 2) the chemical and physical properties of the substrate surface play a key role during the build-up of the organic layer. When an organic crystal is growing, significant changes (due to desorption, molecular readjustment, roughness variation, layer erosion, etc.) occur in the freshly deposited surface. Unfortunately, in-situ and real time spectroscopies are not yet commonly applied to monitor this complex phenomenology; 3) an effective thermodynamic strategy during the arrangement of the organic etero-junction -as in inorganic Molecular Beam Epitaxy- (e.g., control of substrate temperature and sample growth rate, choice of single or multi-bunch growth, etc.) is still lacking in the deposition process. As a matter of fact, only recently a true all-organic epitaxy has been achieved. In this talk, the successful work and the most representative results we obtained in the last five years will be presented, showing that concrete possible solutions to the above mentioned points have been found. In particular, we have succeeded in growing different single organic crystals, namely α-quaterthiophene (α-4T), α-sexythiophene (α-6T), tetracene, rubrene, etc., with different shape, size (up to several square mm's) and orientation. An accurate investigation of the morphological and optical properties of the bare substrate as well as of the freshly grown ultra-thin organic layers has been performed. Our results demonstrate that the organic layer exhibits a high sensitivity to very low amount of contaminants. Moreover, we will show that is possible to tune the crystal growth from a Stransky-Krastanov to a Frank-van der Merve mode during the layer deposition of different organic compounds [α-4T, α-6T, tetracene, rubrene, etc.] by Organic Molecular Beam Epitaxy. In conclusion, the growth of various organic heterojunctions with epitaxial quality is now a gain result.

11:20am **BO+AS+BI+NC-WeM11 Modification of Self-Assembled Monolayer Surfaces Using Hyperthemal Ion Beams**, ***J. Laskin***, *P. Wang*, *O. Hadjar*, Pacific Northwest National Laboratory **INVITED**

Collisions of ions with surfaces play an important role in a variety of scientific disciplines including surface science, materials science, mass spectrometry, imaging and spectroscopy. This presentation will focus on phenomena that occur during collisions of complex polyatomic ions with surfaces at hyperthermal energies with specific emphasis on ion deposition, charge transfer, bond making and bond breaking processes. Because in this energy regime the initial kinetic energy of the ion is commonly sufficient for breaking chemical bonds on the surface but is too low for significant penetration of a polyatomic ion into the surface, hyperthermal collisions are well suited for chemical modification of the outer layer of the surface without substantial perturbation of the bulk substrate. In addition, careful control of the properties of the ion beam can be used for very specific surface modification. Covalent and non–covalent immobilization of peptides using soft-landing of mass-selected ions onto inert and reactive self-assembled monolayer surfaces will be discussed. Fundamental principles derived from such studies are relevant to the understanding of the transport of biomolecules through membranes in living organisms and provides a clear pathway for highly-selective preparation of biological surfaces.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+AS+BI-WeA

Advances in Surface Analytical Methods for Organic and Biological Interfaces

Moderator: D.W. Grainger, University of Utah

1:40pm **BO+AS+BI-WeA1 In-situ Broadband Sum-Frequency Spectroscopy of Biomolecules at Interfaces**, ***P. Koelsch***, *V. Kurz, R. Schmidt,* University Heidelberg, Germany, *C.L. Howell,* University of Maine, *M. Grunze*, University Heidelberg, Germany

Sum-frequency generation (SFG) spectroscopy has been employed to characterize a variety of biointerphases in extended spectral regions in aqueous environment. This contribution summarizes our recent SFG studies on DNA films, extracellular matrix compounds, switchable self assembled monolayers, and other biological molecules. Molecular level details revealed in these studies show that SFG offers the prospect of characterizing conformation, orientation and ordering of biological molecules at interfaces in situ. The technique of SFG spectroscopy is inherently surface specific having submonolayer resolution. Being an all-optical technique it can be operated in aqueous environment and even buried interfaces can be assessed. However, beside the obvious potential impact of SFG spectroscopy, to date, most studies of biological systems have only been performed in the CH and OH stretching vibration regions. This is related to the difficulties in generating tunable high energy light pulses with table top laser systems at the biologically relevant lower wavenumber region (amide and fingerprint) to gain SFG spectra with reasonable signal to noise ratios. In this contribution we show, that our broadband femtosecond SFG spectrometer provides spectral data in the amide I and fingerprint region in air and aqueous environment on a daily bases which opens the opportunity to characterize in situ orientation and conformation of a wider class of more complex biomolecules. We will summarize these biologically related SFG results and demonstrate the potential impact of this technique, also to introduce SFG spectroscopy as another method for examining biofilms ex situ and in situ.

2:00pm **BO+AS+BI-WeA2 Secondary Protein Structures in Barnacle Cement**, ***D.E. Barlow,*** Nova Research, *G. Dickinson, B. Orihuela, D. Rittschof,* Duke University Marine Laboratory, *K.J. Wahl*, U.S. Naval Research Laboratory

Understanding the chemistry of barnacle adhesion is of great interest in the areas of marine biofouling prevention and materials science of adhesives. While most work on the chemistry of barnacle adhesion to date has focused on identifying the protein composition of barnacle cement, relatively little has been done to directly characterize structure of barnacle cement proteins in their native states. Such studies should provide further insight into relationships between chemical structure and adhesion, as well as the types of biochemical mechanisms that may play roles in barnacle cement curing. We have used atomic force microscopy (AFM), circular dichroism (CD), and Fourier transform infrared (FTIR) spectroscopy to characterize cements deposited on quartz and CaF_2 substrates in seawater by barnacles (Amphibalanus amphitrite) transferred from silicone release panels. AFM imaging consistently shows that secondary cement residues left on the substrates are fibrillar. Circular dichroism spectra of cement residues on quartz showed negative peaks centered near 225 nm and positive peaks at about 195 nm, indicating that the barnacle cements are primarily helical in structure, but also contain some β-sheet components. This is further confirmed by transmission FTIR of cement residues on CaF_2, for which the amide III band is found to be composed of a broad band centered ~ 1650 cm^{-1} consistent with α-helical structures, and components near 1685 and 1630 cm^{-1} consistent with β-sheet structures. These results suggest that the fibrillar structures are predominantly helical in structure, in contrast with fibrillar structures like amyloids that exhibit primarily β-sheet conformations.

2:20pm **BO+AS+BI-WeA3 Analysis of Biosamples with Imaging TOF-SIMS**, ***H. Nygren***, *P. Malmberg*, University of Gothenburg, Sweden **INVITED**

Secondary ion mass spectrometry (SIMS) is based on the acceleration of primary ions onto a target. Secondary electrons, neutrals and ions are emitted from the target reflecting its chemical composition. SIMS is unique in its ability to detect simultaneously several target molecules in compound samples and to image their localization at subcellular resolution. The aim of the project is to develop the technology of imaging TOF-SIMS as a tool in biomedical research for analysis and localization of relevant target molecules e.g. inorganic ions, lipids, drugs, carbohydrates and proteins in the same sample. Recent research in TOF-SIMS has shown the distribution of a wide variety of compounds in biological tissue. The current issues in TOF-SIMS analysis are the data interpretation and identification of all new peaks detected with this technique. Until 2004, only a few high mass peaks of biological origin were identified, which leaves us in a situation where much of the interpretation of spectra remains to be done. The aim of this presentation is to define analyte molecules by mass spectra obtained using new primary ion sources with unique fragmentation properties. The possibility to detect proteins is of special interest. It is also an aim of the project to educate students in the analysis of cells and tissue with a high technology method as the research group is presently purchasing our own TOF-SIMS instrument.

3:00pm **BO+AS+BI-WeA5 A Laser Desorption Vacuum Ultraviolet Postionization Imaging Mass Spectrometer for Biological Sample Analysis**, *J.F. Moore,* MassThink LLC, *A. Akhmetov, G.L. Gasper,* University of Illinois at Chicago, *R. Carlson,* Montana State University, *M. Blaze,* ***L. Hanley***, University of Illinois at Chicago

Creating images with mass spectrometry (MS) at <10 micron scale resolution is a substantial challenge due to diffusion effects and low signal levels. A new instrument is described for laser desorption and in-source postionization (LDPI) imaging mass spectrometry with enhanced performance over the previous non-imaging instrument.[1] A significant fraction of the desorbed molecules are intercepted by a vacuum ultraviolet (VUV) postionizing laser, then extracted into the time-of-flight (TOF) mass analyzer. Postionization provides a higher and more consistent sensitivity than matrix-assisted laser desorption/ionization for certain analytes, thereby enhancing imaging MS on this small length scale. The instrument utilizes 349 nm laser desorption with 5 micron minimum spot size, 157 nm laser postionization and will operate at ~200 Hz. Samples are analyzed in microprobe mode and are imaged by rastering the x-y stage. The ion source also incorporates digital optical imaging of the sample surface, which allows for correlation of MS and optical images. The orthogonal geometry of the ion source provides for good separation of direct ion signal and postionized signal by varying the extraction delay, leading to enhanced mass resolution. Use of LDPI-MS is demonstrated for the detection of antibiotics within intact bacterial biofilms.[2] Staphylococcus epidermidis is a common Gram positive bacterium that resides on human skin and is one of the most frequent culprits behind hospital acquired biofilm infections. Treatment of biofilm infections is hindered by the limited ability of antibiotics to kill biofilm associated microbes. LDPI-MS is used to detect antibiotics within intact biofilms without significant interference from other biofilm chemical constituents. Sulfadiazine is detected these biofilms at relatively high concentrations while tetracylcine is detected at near clinical concentrations. These results indicate that imaging MS of bacterial biofilms, animal tissue, or other biological samples by LDPI-MS can be applied to analysis of low ionization potential analytes such as the described antibiotics and other compounds including pharmaceuticals.

[1]M. Zhou, C. Wu, A. Akhmetov, P.D. Edirisinghe, J.L. Drummond and L. Hanley, J. Amer. Soc. Mass Spectrom. 18, 1097 (2007).

[2]G.L. Gasper, R. Carlson, A. Akhmetov, J.F. Moore and L. Hanley, Proteom. (2008) in press.

4:00pm **BO+AS+BI-WeA8 3D Mass Spectrometric Analysis of Non-Dehydrated Biological Samples**, ***H.F. Arlinghaus***, *J. Möller, C. Kriegeskotte, D. Lipinsky*, Westfälische Wilhelms-Universität Münster, Germany

ToF-SIMS and laser-SNMS are increasingly important tools for analyzing the elemental and molecular distribution in biological samples. However, in-vivo analyses of tissues or cell cultures are impossible because the sample must accommodate the vacuum conditions of the instrument. Thus, fixing the sample in its vital state, such as freezing, is essential. Sample preparation by cryo-fractioning or cryosectioning techniques followed by freeze-drying has been successfully used. However, these techniques exhibit several limitations. In order to overcome these limitations, a combination of a ToF-SIMS/laser-SNMS instrument and an in-vacuum cryosectioning instrument were developed for directly preparing and analyzing frozen non-dehydrated samples. The correct sample temperature after preparation and during the analysis showed to be a major factor for the quality of suitable ToF-SIMS/Laser-SNMS analyses. On the one hand, it is necessary to keep the sample cold to avoid freeze drying, on the other hand, a slight increase of the sample temperature removes adsorbates formed by residual gas in the cutting chamber and, more importantly, water resulting from the cutting process, and anticipates adsorption during the analysis. In our presentation, we will show and discuss how to optimize the sample's temperature, sample preparation techniques for analyzing various biological samples, and the possibility of obtaining 3D molecular images of frozen non-dehydrated biological samples. Our data will show that both TOF-

SIMS and Laser-SNMS are capable of imaging elements and molecules in complex biological samples and that they are very valuable tools in advancing applications in life sciences.

4:20pm **BO+AS+BI-WeA9 Construction of Complex Two- and Three-Dimensional Nanostructures: Combined Time-of-Flight Secondary Ion Mass Spectrometry and Microscopy Studies**, *C. Zhou, P. Lu,* ***A.V. Walker***, Washington University in St. Louis

Methods for the chemically selective deposition of metals, semiconductors, biomolecules and other compounds have been studied and applied to the construction of complex multilayer structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. To illustrate our approach we present two examples: the chemical bath deposition (CBD) of zinc sulfide on functionalized SAMs and the construction of three-dimensional nanostructures via layer-by-layer growth. CBD is a solution-based method for the controlled deposition of semiconductors. ZnS is a direct band-gap semiconductor used electroluminescent devices and solar cells. Two sizes of crystallites are observed to form: ~500 nm nanoflowers and ~2 µm crystallites. Nanoflowers nucleate at Zn(II)-carboxylate terminal group complexes on -COOH terminated SAMs. They grow via an ion-by-ion reaction pathway and remain chemically bound to the SAM. In contrast, the micron-sized crystallites form in solution (cluster-by-cluster growth) and are observed on all SAMs studied (-OH, -COOH and -CH_3 terminated SAMs). These crystallites can be easily removed from the surface using sonication. Thus under the appropriate experimental conditions ZnS can be selectively deposited onto -COOH terminated SAMs. We illustrate this by selectively depositing ZnS on a patterned -COOH/-CH_3 terminated SAM surface. Our approach for the construction of three-dimensional nanostructures begins with a single SAM layer deposited and UV-photopatterned using standard techniques. A second layer is then assembled by specific chemical reaction with the terminal groups of the first SAM. Additional layers are deposited using the same method. Experiments to date have focused on the specific coupling reaction of amines with carboxylic acids to form multilayer structures. Using TOF SIMS imaging we have followed each step of this reaction and have been able to demonstrate the selective formation of multilayer structures on patterned -COOH/-CH_3 surfaces. This coupling is used to make several proof-of-concept multifunctional structures.

4:40pm **BO+AS+BI-WeA10 TOF-SIMS Analysis of Lipid Transfer between Vesicles and Supported Lipid Bilayers on TiO_2**, ***P. Sjovall***, SP Technical Research Institute of Sweden, *A. Kunze, B. Kasemo, S. Svedhem*, Chalmers University of Technology, Sweden

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to investigate the electrostatically driven lipid transfer between negatively charged vesicles (POPS) and a positively charged supported lipid bilayer (POEPC) on a TiO_2 surface. Quartz crystal microbalance with dissipation (QCM-D) was used to monitor the formation of the POEPC bilayer (by vesicle adsorption and rupture), the subsequent interaction with POPS vesicles, and the resulting lipid transfer between the bilayer and the vesicles. In addition, QCM-D showed that SDS treatment of the bilayer after lipid transfer removed mass corresponding to one of the lipid leaflets (seemingly leaving a lipid monolayer), and that a bilayer could be reformed upon POEPC vesicle adsorption on this monolayer. TOF-SIMS analysis using Bi_3^+ primary ions was used to provide quantitative estimates of the lipid composition in the different lipid layers. The lipid bilayers were prepared for TOF-SIMS analysis by plunge freezing and freeze drying(1). In order to allow for unambiguous detection of POPS in the lipid bilayers, POPS with fully deuterated palmitate fatty acid tail groups was used in the buffer vesicles. Quantitative estimates of the lipid compositions were made based on the signal intensities from the deuterated (POPS) and undeuterated (POEPC) palmitate ions, as well as from the oleate (POPS and POEPC) ion, using a simple model for the concentration-dependent TOF-SIMS signal intensities. Reference bilayers prepared with known lipid compositions were analysed in order to provide calibration points for the quantitative analysis. The results show that the POEPC bilayer after lipid transfer contains approximately 50% POPS, while the SDS-resistant monolayer contains about 70% POPS and the reformed bilayer contains 20-25% POPS. Possible asymmetries in the lipid composition of the bilayers were, however, not taken into account. A number of peaks, which can be assigned to molecular ions of POPS, were observed in the negative ion spectra of the POPS-containing lipid bilayers. Interestingly, these peaks were absent in the spectra from the SDS-resistant monolayer, although the signal from the deuterated palmitate ion indicated about 70% POPS in the monolayer. This suggests that the POPS molecular peak only shows appreciable intensity in TOF-SIMS spectra from the bilayer structure, similar to what has been observed previously for POPC.[1]

[1]Prinz et al., Langmuir 2007, 23, 8035-8041.

5:00pm **BO+AS+BI-WeA11 Spatial Distribution Analysis of a Selenium Based Anti-Cancer Drug in Tumor Tissue Samples by ToF-SIMS**, ***S.A. Burns***, University at Buffalo, *M. Khin, L. Kazim, Y. Rustum, S. Cao, F. Durrani,* Roswell Park Cancer Institute, *J.A. Gardella*, University at Buffalo

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has recently found new applications in the field of tissue analysis due to the advancement of cluster ion sources.[1] Bi cluster primary ion sources have been shown to produce chemical images with high spatial resolution, to ca. 100nm. The use of C60 cluster ion sources for depth profile analysis distributes the ion impact force allowing for a more specialized analysis of organic samples.[2] ToF-SIMS is an extremely useful application to detect low molecular weight drugs within a polymeric membrane. This study utilized this application to spatially image drug distribution of an anticancer agent in a two types of tissue samples. Nude mice implanted with human head and neck tumors were treated with methylselenocystein (MSC), a known anticarcinogen.[3] MALDI imaging has been used to determine the distribution of another anti-cancer drug, CPT-11 when MSC has also been introduced.[4] The distribution of CPT-11 was found to be more even throughout the tumor in the presence of MSC. This indicates that the MSC causes an increase the vasculature of a tumor thereby allowing other anti-cancer drugs to distribute evenly. MALDI imaging was able to show drug distribution but could not associate the fragment peak of the MSC with the vasculature of the cells due to restrictions in image resolution (100µm). ToF-SIMS imaging has been shown to reach resolutions of 100nm allowing for this type of analysis to be performed. MSC treated tumor and liver samples were analyzed using imaging and depth profiling to determine the distribution of drug with respect to the vasculature of the tissue. The first step of this study was to determine characteristic peaks from the MSC that could be identified in the tissue samples. Analysis of the livers and tumors of the mice that had been treated with MSC had fragment peaks with isotopic distributions indicating selenium containing organic compounds not found in the control samples. These fragment peaks were used as the drug peaks whose distribution in the tissue samples were compared to fragment peaks which could be attributed directly to cell vascular structure.

[1]Brunelle,A,et al. Journal of Mass Spectrometry 2005,40,985-999
[2]Fletcher,JS,et al. Analytical Chemistry 2006,78,1827-31
[3]Azrak,RG,et al. Biochemical Pharmacology 2007,73,1280-1287
[4]Prieto Conaway,MC,et al. Thermo Scientific 2008,Application Note.

5:20pm **BO+AS+BI-WeA12 Effects of Different Sample Preparation Methods for Cell Imaging using TOF-SIMS**, ***J. Malm***, SP Technical Research Institute of Sweden, *D. Giannaras*, University of Glasgow, UK, *P. Sjövall,* SP Technical Research Institute of Sweden, *N. Gadegaard, M.O. Riehle*, University of Glasgow, UK

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is increasingly being used for chemical imaging of cells and tissue. A concern in these studies is that the samples need to be prepared for the vacuum environment. Several sample preparation methods exist for this purpose. In this work, effects of different preparation methods on the structure and surface chemistry of human fibroblast hTert cells were studied. Two fixation protocols, using glutaraldehyde (GA, $C_5H_8O_2$), and osmium tetroxide (OsO_4), respectively, were compared to a non-fixing protocol where cells were washed with ammonium formate (AF, NH_4HCOO) prior to drying. Three drying techniques were compared, namely freeze-drying (FD) after rapid plunge-freezing, critical point-drying (CPD), and alcohol ladder-drying (ALD). Imaging TOF-SIMS with Bi_3 cluster primary ions was used to compare the different preparation protocols with respect to surface chemistry, and the structure of the cells after preparation was studied using scanning electron microscopy (SEM). For the AF-washed samples, changes in cell volume was followed by interference reflection microscopy (IRM). The results show that both the fixation/washing protocols as well as the drying protocols affect the chemical information obtained in TOF-SIMS analyses. For GA-fixed samples, both CPD and ALD give rise to reduced phosphocholine (PC) signal on the cell surface by two orders of magnitude, as compared to FD, while no significant differences are seen for cholesterol and amino acid fragment ions. GA-fixed samples post-fixed using OsO_4 showed PC intensities reduced by only one order of magnitude, going from FD to CPD or ALD. The cholesterol intensity was found to be higher for AF-washed cells and cells fixed with OsO_4, than for GA fixed cells. An increase in amino acid intensity going from AF to GA to OsO_4 was also observed.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+EM+BI+NC-ThM

Semiconducting Biointerfaces and Sensors
Moderator: L.J. Brillson, Ohio State University

8:00am **BO+EM+BI+NC-ThM1 AlGaN/GaN HEMT And ZnO Nanorod Based Sensors for Chemical and Bio Applications**, *B.S. Kang, H.T. Wang, K.C. Chen, Y.L. Wang, T. Lele, J. Lin, S.J. Pearton,* ***F. Ren***, University of Florida

AlGaN/GaN high electron mobility transistor based sensors are good candidates for low cost, handheld, and wireless chemical and biomedical sensor due to their excellent thermal as well as chemical stability and sensitivity to the changes of ambient. The electrons in the AlGaN/GaN HEMT two-dimensional electron gas (2DEG) channel are induced by piezoelectric and spontaneous polarization effects and there is no dopant needed. There are positive counter charges at the AlGaN surface layer induced by the 2DEG. Any slight changes in the ambient of the AlGaN/GaN HEMT affect the surface charges of the AlGaN/GaN HEMT. These changes in the surface charge are transduced into a change in the concentration of the 2DEG in the AlGaN/GaN HEMTs. We have demonstrated AlGaN/GaN HEMT based individual sensors for protein, DNA, kidney injury molecules, prostate cancer, pH values of the solutions, pH in the exhaled breath condensate, and mercury ions with specific surface functionalizations. We have also demonstrated ZnO nanorod based sensors to detect UV, hydrogen, carbon monoxide and ammonium. Recently, we integrated ZnO nanorods with AlGaN/GaN HEMT to detect glucose in the breath condensate. This approach makes a possibility of integrating AlGaN/GaN HEMT based sensors with ZnO nanorod sensors on a single "smart sensor chip" with the techniques of selective area functionalization and mircofluidic device approaches. This smart sensor chip can be mounted on a handheld, portable, wireless transmitter circuit board.

8:20am **BO+EM+BI+NC-ThM2 Label-Free Dual Sensing of DNA-Molecules using GaN Nanowires**, ***A. Ganguly***, *C.-P. Chen*, National Taiwan University, *K.H. Chen*, Academia Sinica, Taiwan, *L.C. Chen*, National Taiwan University

GaN, a leading optoelectronic material, is also known to be non-toxic and bio-compatible. Interestingly, this material in the form of nanowires (NWs), with the advantages of large surface-to-volume ratio and direct electrical-path due to surface-induced spatial-separation of charge-carriers, could possess high sensitivity to the local environment, hence to the surface-immobilized biomolecules. Here, we report the GaN NWs possess high bio-binding efficiency and provide a platform for in situ, label-free, and rapid (assay-time within 2 hours) detection of DNA-molecules with dual-sensing capability (electrochemical and optical). Both electrochemical (EC) and optical (photoluminescence, PL) measurements showed clear distinction of pristine GaN NWs with probe-DNA (pLF) immobilization, and after further hybridization, employing a popular target-DNA with anthrax lethal factor sequence (LF). In label-free condition, both EC and PL-based techniques exhibited high sensitivity, without any little effort to optimize the sensing-condition, up to nM and pM of concentrations, respectively for the recognition of LF, with very low assay-time. Furthermore, successful application for detection of "hotspot"-mutations, related to human p53 tumor-suppressor gene, revealed excellent selectivity and specificity towards the fully-complementary targets, down to pM concentration, even in presence of mutations and non-complementary strands, suggesting the potential pragmatic application in complex clinical samples. The simplicity in detection-method, without any requirement of extra step/modification in both probe and target-systems, and simultaneously, the unique label-free dual-detection capability of GaN NWs, with excellent selectivity and sensitivity, can make them a promising choice of transducers, even in clinical application.

8:40am **BO+EM+BI+NC-ThM3 GaN Field Effect Transistors for Biosensor Applications**, ***W. Lu***, The Ohio State University **INVITED**

Biosensors based on electrical field effect transistors (FETs) are of great research interests due to their properties of label free, low cost, small size, and easy integration to external circuitry electronics. Such biosensors have been fabricated on many semiconductor materials including Si, silicon on oxide, carbon nanotube, ZnO, etc. Si-based such biologically FETs (bioFETs) suffer from various difficulties such as limited sensitivity and current drift caused by degradation of gate dielectrics and chemical instability. Due to the chemical inertness and the high concentration of two dimensional electron gas (2DEG) at the AlGaN/GaN interface, AlGaN/GaN heterojunction FETs have great potentials for detection of bioagents in biological buffers with high ionic strengths. In this paper, we will give an overview of recent research progress on GaN FET biosensors. The process and characterization of functionalization of AlGaN surface for biosensing applications will be discussed. The detection of streptavidin (STA) and monokine induced by interferon γ (MIG) proteins and hybridization process of single strand DNAs by AlGaN/GaN HFETs will be presented. Specifically, for STA detection, at different ionic strengths, the effect of Debye length on detection sensitivity has been demonstrated. No current change is observed for fully biotinylated STA, indicating that there is no non-specific binding. Furthermore, we have used open binding pockets of specifically-bound STA on the biotinylated surface as receptors for detection of biotinylated MIG proteins. The results show that the devices are capable of detecting of biotinylated MIGs at pathological concentrations even at physiological ion strengths. In part, this is due to the superior stability of the AlGaN/GaN HFET platform in buffer, which results in sensor noise being sufficiently low to allow reproducible detection of protein analyte binding. For comparison, regular unbiotinylated MIG proteins gave no current change, indicating that there is no non-specific binding and the change of current is due to the charges transferred from charged analytes.

9:20am **BO+EM+BI+NC-ThM5 Surface Functionalization of ZnO Nanoparticles and Thin Films for Sensor Applications**, ***L. Selegard***, *C. Vahlberg, F. Söderlind, V. Khranovskii, A. Lloyd Spetz, R. Yakimova, P.-O. Käll, K. Uvdal*, Linköping University, Sweden

A new procedure has been developed for functionalization of electrochemically produced ZnO nanoparticles. The core of the particles was characterized using TEM, PEEM and LEEM. Single crystal nanoparticles, with uniform spherical morphology with a size of approximately 50Å were obtained. The first aims of ZnO nanoparticle functionalization were to make a stabilizing molecular layer at the surface and to prepare for further linking possibilities, for use in different types of sensing applications. The functionalization process was investigated and the molecular layer was verifyed by XPS and FT-IR. Parallel studies on biofunctionalization of plane ZnO thin films were performed to obtain a suitable reference system. One of the molecules used for functionalization of the nanoparticle surface was (3-Mercaptopropyl)triethoxysilane (MPTS) as it enables further functionalization on the thiol part and as it has the possibility to form a stable network around the particles. The MPTS linking was investigated by XPS and NEXAFS. The XPS spectra of the functionalized particles showed significant signal from both Si and S verifying the presence of MPTS. XPS core level S2p spectrum further showed presence of SH groups, indicating that thiols was available for further linking processes. Another molecule of interest for nanoparticle functionalization is oleic acid. The strategy is then to coordinate the carboxyl groups to the surface and further linking will be based on hydrofobic interactions. The TEM and PEEM results, so far, indicated that the particles were not fully dispersed but the use of oleic acid showed a much smaller extent of agglomerated particles than for example MPTS. PEEM also showed that the oleic acid capped particles was much more heat stable then MPTS capped once. ZnO nanoparticles show two emission peaks, one band gap related UV-emission and one visible emission arising from oxygen vacancies. In this work fluorescence spectroscopy was used to study the emitted, visible light of the particles as a function of different surface modifications.

9:40am **BO+EM+BI+NC-ThM6 Surface Functionalization and Micropatterning of Ta_2O_5 Films Using Organo-silane and Atom Transfer Radical Polymerization(ATRP) Methods**, ***W. Kulisch***, *D. Gilliland, G. Ceccone, L. Sirghi, F. Rossi, H. Rauscher*, European Commission Joint Research Center, Italy

Optical waveguide biosensors frequently require the use high refractive index thin films such as tantalum pentoxide to act as both as a light guide and as a surface on which active biomolecules can be covalently immobilized. In this work, a process for the room temperature deposition of Ta_2O_5 films onto silicon/silica and thermoplast substrates by reactive ion beam sputtering from a tantalum target has been developed. The resultant high refractive index films have been chemically and optically characterized and methods examined for the wet chemical modification of the oxide film to produce either reactive amino groups or low protein fouling polyethylene glycol (PEG) layers. In both cases the first step toward the functionalization of the as-grown films used either an oxygen plasma or to an UV/O_3 treatment to produce a clean and fully oxidized surface. Using these clean, active surfaces-NH_2 terminated SAMs could be routinely produced using a conventional silanization process using 3-aminopropyl trimethoxysilane (APTMS). To produce high density, low protein binding (anti-fouling)

layers a more sophisticated procedure based on surface initiated atom transfer radical polymerization (SI-ATRP) of poly(ethylenglycol)methacrylate (PEGMA) has been used. In this method the oxide surface is firstly modified using a combination of poly(glycidylmethacrylate) (PGMA) and α-bromoisobutyryl bromide (BIB) to produce a surface rich in tethered α-bromoisobutyryl groups. These BIB groups can then used as initiation sites for the growth of dense PEG films using the copper complex catalysed ATRP of PEGMA macromonomers. To characterize the final surfaces and to assist in the optimization of process, time-of-flight secondary ion mass spectrometry (TOF-SIMS), X-ray photoelectron spectroscopy (XPS), contact angle measurements and atomic force microscopy (AFM) have been applied to samples after each step of the different processes. The effectiveness of the two processes will be demonstrated and examples given of methods by which the two methods have been combined for the production of fouling/non-fouling micropatterned surfaces.

10:40am **BO+EM+BI+NC-ThM9 Designing the Interfaces between Biomolecules and Semiconductor Substrates: From the C60 Buckyball Model System to Shape-Restricted DNA Molecules**, ***X. Zhang***, *A.V. Teplyakov*, University of Delaware

A well-characterized interface based upon covalent binding between biomolecules and semiconductor surface was designed using the functionalized self-assembled monolayers (SAM) on Si(111) surface and specific shaped-restricted DNA molecules. This type of interface can serve as a prototype for the future devices in biosensing and single molecule spectroscopy. The spectroscopic and microscopic benchmarks were initially tested using fullerene C60 as a model to understand the attachment chemistry of large molecules with amine-terminated SAM on Si(111) surface. X-ray photoelectron spectroscopy (XPS) and Infrared spectroscopic (IR) studies, supported by computational investigation, verified the covalent attachment of C60 to the amine-terminated SAM on Si(111) surface. The atomic force microscopy (AFM) revealed the topography of the C60-modied surface with molecular resolution. The biomolecule/semiconductor interface was tailored with the same amine-terminated SAM on Si(111) surface and thiol-DNA molecules, which is achieved via a sulfo-succinimidyl 4-(N-maleimidomethyl)-cyclohexane-1-carboxylate (SSMCC) crosslinker molecule. The shape-restricted thiol-DNA is anchored to the surface through the formation of covalent bonds as confirmed by XPS and time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The AFM is used to visualize the well-defined and selective covalent binding of thiol-DNA molecules on SAM-covered Si(111). In addition, AFM and contact angle measurement are employed to study the change of the surface topography and the change of the surface hydrophilicity following each step of the DNA attachment chemistry on silicon.

11:00am **BO+EM+BI+NC-ThM10 The Effect of a Spacer Thiol on the Orientation and Hybridization Properties of 40mer DNA SAMs on Gold**, ***L.J. Gamble***, *P.-C. Nguyen, T. Weidner,* University of Washington, *D.W. Grainger,* University of Utah, *D.G. Castner*, University of Washington

Methods for surface-immobilizing single-strand nucleic acids while preserving their original hybridization specificity with minimal non-specific interactions remain an important goal for improving the performance of surface bound DNA microarray and biosensor applications. Before the full potential of DNA microarrays can be realized, fundamental issues must be better understood, including how the crowding, conformation and orientation of immobilized DNA impacts DNA target hybridization efficiency. For detection of small amounts of DNA in a target solution, the coverage and orientation of DNA probes should be optimized for the capture of low concentrations of DNA via hybridization. In this study the effect of backfill of mercaptohexanol (MCH) on 40mer thiolated single stranded DNA (SH-ssDNA) sequence orientation and hybridization efficiency is studied with X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, sum frequency generation (SFG) vibrational spectroscopy, and surface plasmon resonance (SPR). While XPS and NEXAFS are both ultra-high vacuum techniques, SPR is a real-time solution based technique and SFG spectroscopy can be acquired both at the solid-air interface as well as the solid-liquid interface. While the 40mer DNA is longer and expected to be more disordered, the NEXAFS N k-edge spectra showed increased the polarization dependence of the peaks at 401eV and 399eV for the 40mer sequence increased with an MCH backfill time of 1 hour. SFG spectroscopy results showed that incorporation of the MCH into the DNA monolayer resulted in an increase of the nucleotide related peaks at 2961 cm^{-1} and 3045 cm^{-1} which maximized at 1 hour MCH backfill. This evidence of orientation changes in the surface bound 40mer DNA will be correlated with hybridization data from SPR.

11:20am **BO+EM+BI+NC-ThM11 Anchoring and LT-STM/STS Characterization of Single Organic Molecules at Semiconducting and Insulating Surfaces**, ***M. Szymonski***, *A. Tekiel, S. Godlewski, G. Goryl, J. Prauzner-Bechcicki, J. Budzioch*, Jagiellonian University, Poland

In recent years self-assembling of organic molecules deposited onto different surfaces have attracted considerable attention because of important applications in organic electronic technologies and prospects for development of single molecule computing devices. In this presentation we will report on our recent studies of initial stages of growth and organization of several organic molecules on reconstructed (001) surface of InSb, (011) and (110) surfaces of TiO2, and on ultrathin KBr layers grown epitaxially on InSb(001). Among different organic molecules the perylene derivative - 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA), often regarded as a model system for planar-stacking molecules, copper phthalocyanine (CuPc), violet landers (VL), and chiral helicene[11] molecules were studied by means of scanning tunneling microscopy (STM) at room and liquid nitrogen temperatures, nc-AFM at room temperature and low energy electron diffraction (LEED). It is shown that during initial stages of growth on InSb molecules often form chains parallel to [110] crystallographic direction of the c(8x2) reconstructed substrate. They are frequently attached to the lower terrace step edge, or some defects on the surface, indicating surprisingly weak interaction between the molecules and the substrate and their high mobility along [110] diffusion channel. Geometrical orientation of the molecules with respect to the reconstruction rows of the substrate will be discussed. We will present the images acquired with submolecular resolution, as well as images demonstrating the pinning effect of the molecular chains by surface charge density waves, and incorporation of the molecules into overall electronic structure of the system.

11:40am **BO+EM+BI+NC-ThM12 Molecular Self-Assembly of Funtionalized Fullerenes on a Closed Packed Metal Surface**, ***B. Diaconescu***, University of New Hampshire, *T. Yang, S. Berber,* Michigan State University, *M. Jazdzyk, G. Miller,* University of New Hampshire, *D. Tomanek,* Michigan State University, *K. Pohl*, University of New Hampshire

Self-assembled organic thin films have a great number of practical applications, ranging from sensors and biological interfaces in medical implants to organic electronics and photovoltaics. Generally speaking, self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule–substrate and intermolecular interactions. Therefore, to control such self-assembly processes in a useful way, it is mandatory to understand how this balance reflects onto the SAM's final structure. Here, we present a combined STM and DFT study of the self-assembly of C60 molecules functionalized with long alkane chains, F-C60, on the (111) surface of silver. We find that F-C60 molecules lay down on the Ag surface and form a complex zigzag like pattern with an oblique unit cell of 4 nm by 2.5 nm and two molecules per basis. The C60s are placed at a larger than van der Waals distance. The symmetry of the functionalized C60 self-assembled monolayer is dictated by the alkane–surface interaction while the size of the unit cell is a consequence of the in-plane intermolecular interactions. These results show that C60s can be assembled in a two-dimensional and non-compact molecular array and suggest a way to control their surface density via appropriate chemical functionalization.

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Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+NS+BI+NC-ThA

Biological and Molecular Applications of Nanostructures

Moderator: P. Kingshott, The University of Aarhus, Denmark

2:00pm **BO+NS+BI+NC-ThA1 Fabrication of Nanoscale Bioarrays for the Study of Cytoskeletal Protein Binding Interactions Using Nano-Imprint Lithography**, ***M. Schvartzman***, *M. Palma, J. Abramson, J. Sable, J. Hone, M.P. Sheetz, S.J. Wind*, Columbia University

Recent advances in solid-state nanofabrication technology now make it possible to fabricate structures in the size regime of biomolecules, i.e., ~ tens of nanometers and below. We are developing a system that mimics biological spatial order by using nanofabricated structures which are organized into hierarchical arrays in which structural parameters, such as spacing and orientation, are systematically varied, and which provide multiple protein binding sites with nanometer-scale separations. The aim of the work is to study the dependence of large cytoskeletal protein binding on the geometrical arrangement of extracellular matrix (ECM) proteins and integrins. Nanoscale patterns are formed in arrays containing metal dots 5 - 10 nm in diameter, which are functionalized with linker molecules that specifically interact with individual protein binding sites. These dots can be arranged individually, in pairs, or in more complex patterns based on the structure of the molecules under investigation. In particular, we are interested in understanding of the importance of the spacing between integrin cytoplasmic tails on the binding of other proteins, such as talin, that are involved in the building of focal adhesion (FA) complexes by which the actin cytoskeleton attaches to the ECM. The nano-arrays fabrication process uses thermal nanoimprint lithography and pattern transfer by Au/Pd deposition and lift-off. For the lift-off process for such small features and relatively thin resist layer, an angle evaporated metal hard mask is deposited after the NIL step, followed by resist descum. A post-lift-off annealing step at 400 – 500 oC results in further reduction of feature size and a high degree of uniformity. Spheroidal dots are formed with diameters ~5 - 10 nm. The pattern is functionalized with fibronectin RGD motif through a biotin-avidin-biotin linkage. Total-Internal-Reflectance Fluorescence (TIRF) is used for the monitoring of the bio-functionalization with fluorescene labeled molecules. In-vitro study of cells spreading on the patterned and bio-functionalized surfaces is performed on the patterns with different geometries. This presentation will describe the fabrication arrays of ultra-small metal features using NIL technology, functionalization and implementation of these arrays in the study of the fundamentals of cell behavior, representing a new example of the enormous impact of nanofabrication on the life sciences.

2:20pm **BO+NS+BI+NC-ThA2 Universal Method for Forming Various Metal Particles as Multiplexed Labels for Electron Microscopy in the Backscattering Mode**, ***H. Takei***, *H. Kim, K. Yasuda*, Kanagawa Academy of Science and Technology, Japan

Scanning electron microscopy is a powerful technique in terms of resolution, three dimensional rendition of the object and use of ease. Life science is one among many fields for which SEM is an indispensable tool, and it continues to find new uses. One way to enhance its utility in the field of life science is to multiplex labeling as carried out routinely with fluorescence microscopy; labels with different emission spectra. For this purpose, one approach would be to use particles made from different metals because different metals backscatter electrons differently in accordance to the atomic weight. In the backscattering mode, particles made from different metals can be readily distinguished by the brightness of the image so that labeling each type of the particle with distinct biomolecules such as an antibody or DNA would allow one to observe distributions of distinct molecular species simultaneously, as with multiplexed fluorescence labeling, albeit at much higher resolutions. What is needed is thus a method to produce various metal particles at will. For this purpose, we will demonstrate a universal method consisting of formion of a dense monolayer of monodisperse Latex spheres with a self-assembling technique and then evaporating a metal that can be readily evaporated or sputtered. With the above method, the sphere adsorption is accomplished through mild physisorption so that application of mild sonication to surface bound metal particles in the presence of a liquid such as water leads readily to re-dispersal of Latex sphere coated with the metal. We show that resulting particles made from different metals such as gold, silver, nickel or aluminum can be readily distinguished. The sphere size used ranges typically from 50 to 100 nm with the deposition thickness anywhere between 5 to 20 nm. Beside its flexibility with respect to the type of metal that can be used, another advantage of this method lies with a fact that particles can be surface-modified while still adsorbed on a surface. This is particularly advantageous from the perspective of rinsing after each surface treatment protocol. It should be mentioned that because particles are covered only on one side, two types of surfaces, metal and exposed polystyrene, can be selectively used for surface modifications; if necessary two sides can be modified with two distinct species at the same time to give higher functionalities.

2:40pm **BO+NS+BI+NC-ThA3 Nanoscopic Presentation of Peptides at Cell Interfaces**, *J.P. Spatz*, ***V. Hirschfeld-Warneken***, MPI for Metals Research and U. of Heidelberg, Germany **INVITED**

Engineering of cellular environments has become a valuable tool for guiding cellular activity such as differentiation, spreading, motility, proliferation or apoptosis which altogether regulates tissue development in a complex manner. The adhesion of cells to its environment is involved in nearly every cellular decision in vivo and in vitro. Its detailed understanding and defined control also opens new strategies for medical technologies with respect to, e.g., stem cell regulation, tissue scaffolds, cell selection due to their disease state, artificial blood vessels, or immunology. Our approach to engineer cellular environments is based on self-organizing spatial positioning of single signaling molecules attached to inorganic or polymeric supports, which offers the highest spatial resolution with respect to the position of single signaling molecules. This approach allows tuning cellular material 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 trigger 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. 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.

3:20pm **BO+NS+BI+NC-ThA5 Bioadhesive/Bioresistant Nanopatterns: Fabrication, Characterization and Investigation of Their Effect on Enhancing Biomolecule Affinity Reactions**, ***I. Mannelli***, *A. Valsesia, P. Lisboa, P. Colpo, F. Rossi*, European Commission Joint Research Centre, Italy

Fabrication and characterisation of nanopatterned surfaces are topics of many past and present research studies. Recently many techniques have been investigated for the fabrication of nanopatterned surfaces. Among them colloidal lithography combined with plasma polymer deposition and/or self-assembly has shown to be a flexible technology for producing large area nanostructured surfaces. At the same time investigations have increasingly focused on the behavior of biomolecules (i.e. protein, nucleic acid) when interacting with surfaces and/or particles with nanometre dimensions. Although many studies have been done on the surface/biomolecule interaction mechanisms and the conformation changes that molecules undergo after the interaction with macroscopic surfaces it is much less well understood how the biomolecules interact with surfaces that have been previously functionalised with nanofeatures. In particular little is known about the interactions which occur with features with dimensions comparable with those of the biomolecules themselves and how, after the interaction, the native molecule conformation changes. We have optimized a procedure for fabricating nanopatterned surfaces at the sub500 nm scale in which a hexagonal close packed array of bioadhesive gold nanoareas are embedded in an anti-fouling matrix (PEO-like polymer). The surfaces fabricated in this way were characterized by AFM analysis and their interaction with amino functionalised Au nanoparticles were investigated. The AFM images show the crystalline arrangement of nanopattern array and the localization of the H_2N-Au nanoparticles in the bioadhesive areas. A SPR Imaging system was used to perform kinetics studies on the adsorption and interaction behaviour of biomolecules on these surfaces. At the same time, the detection performance of these surfaces when employed as a transduction platform for studying biomolecule interactions has been investigated. To do this, a recognition biomolecule was immobilized on the surface and the affinity reaction with a specific target molecule was

monitored in real time by means of the SPRi system. The investigated surfaces showed an enhancement of the affinity reaction efficiency with respect to the non structured surfaces. The results obtained show that nanostructuring the surfaces makes it possible to improve the binding site accessibility of the immobilized biological probes without significantly modifying the native biomolecule conformation.

4:00pm **BO+NS+BI+NC-ThA7 Control and Separation of Proteins in a Nanofluidic FET Device, using pH Gradient and Valence Charge**, ***Y.-J. Oh***, University of New Mexico, *D.R. Bottenus, C.F. Ivory,* Washington State University, *S.M. Han*, University of New Mexico

We have fabricated Si multiple internal reflection infrared waveguides embedded with a parallel array of nanofluidic channels (100 nm W ×500 nm D) and studied field-effect-transistor (FET) flow control and separation of proteins, using scanning laser confocal fluorescence microscopy (SL-CFM) and multiple internal reflection Fourier transform infrared spectroscopy (MIR-FTIRS). For fluidic FET, a DC potential is applied to a highly doped gate area in the mid-section of nanochannels, in addition to a longitudinal electric field along the nanochannels. The gate potential controls the surface charge on SiO_2 channel walls and therefore their ζ-potential. Depending on the polarity and magnitude, the gate potential can accelerate, decelerate, or reverse the flow of proteins. In addition, our MIR-FTIR analysis demonstrates that fluorescein dye molecules, used here as a pH indicator, are hydrogenated and dehydrogenated in response to the gate bias and subsequent pH shift. Using fluorescein, we have thus measured a pH shift caused by the surface charge modulation and longitudinal electrical field. We observe that this pH shift is further influenced by water electrolysis occurring at the electrodes that drive the electroosmotic flow as well as at the gate where a leakage current unavoidably flows through a thermal SiO_2 layer. Using this pH manipulation and generating a pH gradient along the nanochannels, we have conducted isoelectric focusing and separation of proteins with different isoelectric points (Ip). In this presentation, we will further discuss protein separations, using transverse electromigration based on their different valence charges in relation to the surface charge on channel walls.

4:20pm **BO+NS+BI+NC-ThA8 High Throughput Device for Surface Modification Studies**, ***S. Saxer***, *S. Tosatti, S. Zuercher,* ETH Zurich, Switzerland, *K. Gademann,* EPF Lausanne, Switzerland, *M. Textor*, ETH Zurich, Switzerland

Surface coatings are often used to control the degree of the interaction between the material and the surrounding environment. Paints and lacquers are the most common and widespread coatings. Recent developments in the process of micro- and nanostructures lead to the demand of thinner coatings, which maintain the aspect ratio and preserve the fine structures. Such conditions can be fulfilled by the use of self-assembled monolayers.[1] Due to the large spectrum of applications are nowadays high-throughput approaches required to screen through a large number of parameters, ranging from the substrate up to the different assembly conditions (temperature, solvent, pH). We designed a surface modification screening platform (SuMo-device), which allows the parallel execution of different surface–modification experiments while allowing a single measure for the adlayers characterization, thus enhancing the efficiency of the experiment. The seventy wells (working area/well: 7mm^2; Volume/well: 20µmL) provided by the SuMo-device, were verified with solutions having different concentrations of the grafted copolymer; poly (L-lysine)-grafted-poly ethylene glycol, which is known to adsorb electrostatic to different metal oxide substrates and to render the surface resistant against non-specific protein adsorption (non-fouling), and thus resulting in adlayers with different coverage and thickness.[2] A secondary adsorption of fluorescein isothiocyanate labeled fibrinogen (FITC-fbg) enables to test the non-fouling behavior and therefore the quality of the polymer layer, by the measurement of the fluorescence with a microarray scanner.[3] A standard evaluation procedure was introduced to enable a quantification of the fluorescent response. The Limit of Detection (LOD) was calculated from the standard curve and requires a minimum FITC-fbg concentration of 0.002mg/mL (incubation: 1 h at 25°C). The fluorescence data were compared and found to correlate with layer thickness (ellipsometry) and with the in situ mass adsorption curve obtained by optical biosensor devices. Thus, we conclude that our approach offers a faster and more efficient way to screen between different possible coatings strategies, similarly to drug discovery processes.

[1] F. Schreiber, Prog. Surf. Sci. 65, 151 (2000)
[2] G.L. Kenausis et al., J. Phys. Chem. B 104, 3298 (2000)
[3] S. Pasche et al., Langmuir 19, 9216 (2003).

4:40pm **BO+NS+BI+NC-ThA9 Nanopatterned Functional Surfaces by Electron Beam Lithography of Plasma Assisted Chemical Vapour Deposited Polymers**, *F. Bretagnol, A. Valsesia,* ***G. Ceccone***, *D. Gilliland, P. Colpo, F. Rossi*, European Commission, Joint Research Centre Italy

We presents a method for the fabrication of well defined chemically active nano-patterned surfaces. Electron-beam lithography is applied on plasma-deposited polymers in order to create sub-micron carboxylic functional areas over a non-bio-adhesive matrix. Characterization of the patterned surface demonstrates that this technique can be used to fabricate chemically active features with lateral size down to 200 nm. Moreover, experiments with a model protein (bovine serum albumin) on the patterned surfaces show preferential adhesion on the active region indicating the ability of this method for the design of biosensing platforms.

5:00pm **BO+NS+BI+NC-ThA10 Application of Plasma Polymerised Microchannel Surfaces for IEF**, ***M. Salim***, *B. O'Sullivan, S.Y. Ow, P.C. Wright, S.L. McArthur*, The University of Sheffield, UK

The emerging proteomics field has triggered the development of many bioanalytical tools and technologies. Since biological samples are usually present in small quantities and volume, there is a high priority for the analytical tools to be able to process these minute samples. The use of microfluidics for this purpose has thus emerged. Plasma polymerisation has been shown to be an attractive method to coat microchannel surfaces. Here, we apply the plasma surface modified microchannels for on-chip IEF protein separation (separation based on the isoelectric points of the proteins). A common problem associated with the use of non-coated glass or fused silica substrates in IEF is the high electroosmotic flow (EOF) and high extent of protein adsorption. Therefore, coated microchannel surfaces are usually introduced to reduce the EOF and reduce protein adsorption, and improve the resolution of the separation. Lower EOF can also permit IEF separation in short channel lengths. In this study, we investigate the applicability of plasma polymerised tetraglyme surface for IEF-facilitated protein separation at a 2.2 cm channel length, since it exhibits slower EOF compared to non-coated microchannel surfaces, and is low-fouling. Comparisons were also made to non-coated microchannels and other types of plasma polymers, i.e. plasma polymerised acrylic acid and plasma polymerised allylamine coated surfaces. IEF performed on the low-fouling plasma polymerised tetraglyme microchannel surface was shown to exhibit better separation compared to non-coated microchannel, as observed from the clearer formation of focused protein bands. Also, due to the presence of protein and carrier ampholytes adsorption in both plasma polymerised acrylic acid and allylamine coated microchannels, these surfaces may not be suitable for IEF protein separation over a wide range of pH, with the separation resolutions decreasing after repeating experimental runs.

5:20pm **BO+NS+BI+NC-ThA11 Plasma Deposited Polyethylene Oxide as a Platform for Proteins and Stem Cells Microarrays**, *L. Ceriotti,* JRC, Ispra, Italy, *L. Buzanska,* JRC, Ispra, Italy and Polish Academy of Science, *H. Rauscher, I. Mannelli,* ***L. Sirghi***, *D. Gilliland, M. Hasiwa, F. Bretagnol, A. Ruiz, S. Bremer, S. Coecke,* JRC, Ispra, Italy, *P. Colpo,* Joint Research Center, IHCP, Italy, *F. Rossi*, JRC, Ispra, Italy

In this work we fabricated and characterized microarrays of proteins of the extra cellular matrix (ECM) for stem cells adhesion studies. Plasma deposited poly(ethylene) oxide (PEO-like) film coated glass slides has been chosen for its dual properties, being protein and cell repellent in wet conditions and protein adhesive in dried conditions. The microarrays were created by direct microspotting of the proteins on the PEO films with optimized printing buffer by using a non-contact printing technology. The stability and the quality of the spots of fibronectin used as model protein were assessed by Time of Flight- Secondary Ion Mass Spectrometry (ToF-SIMS) and ellipsometry was used to determine the amount of protein immobilized on each spot after rinsing of the substrate with water. It was found that when fibronectin is spotted at a concentration higher than 84 µmg/ml, the protein forms a monolayer with a density of 112 ± 4 ng/cm^2 with a low surface coverage but quite regular spatial distribution as confirmed by Atomic Force Microscopy (AFM) measurements. The active conformation of the spotted fibronectin as a function of the spotted concentration was verified by performing an immunoassay with antibodies specific for the fibronectin RGD sequence by Surface Plasmon Resonance (SPR) imaging. Human Umbilical Cord Blood Neural Stem Cells (HUCB-NSCs) were cultured on different ECM protein arrays (fibronectin, laminin, collagen I, collagen III and collagen V) showing a protein type and concentration dependent adhesion and growth on the micro-spots. No cells were found in-between the spots thanks to the anti adhesive properties of the PEO-like film. The cell nuclei were stained for cell counting and preliminary specific cell staining was performed to evaluate the differentiation stage of HUCB-NSCs on fibronectin spots. The array platform developed in this study provides a promising approach to investigate in a high throughput manner how insoluble factors patterned on the surface influence stem cell adhesion and development.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+SS+AS-FrM

Self Assembled Ultrathin Organic Interfaces
Moderator: S.L. McArthur, Swinburne University of Technology, Australia

8:40am **BO+SS+AS-FrM2 Photo-Patterned SAMs on Au(111) and SiO_x: An XPS Investigation**, ***A.M. Track***, University of Graz, Austria, *A. Lex, T. Höfler, T. Griesser, P. Pacher, H.-G. Flesch,* Graz University of Technology, Austria, *G. Hlawacek,* University of Leoben, Austria, *R. Schenach, G. Trimmel,* Graz University of Technology, Austria, *W. Kern,* University of Leoben, Austria, *G. Koller, M.G. Ramsey*, University of Graz, Austria

Self-assembled monolayers (SAMs) can provide a simple, flexible, highly ordered and convenient system to tailor and functionalize surface and interface properties of metals, metal oxides and semiconductors. For instance a simple way to change the chemical reactivity of the substrates is to use organic photosensitive SAMs which will also allow patterning with UV illumination. We focus on the characterization of the reactions occurring in SAMs and thin interfacial layers using X-ray photoemission spectroscopy (XPS). To increase the contrast between the non-illuminated and illuminated SAMs (or thin films) we perform a selective post modification of the patterned films with organic reagents containing heteroatoms. The chemical differences of the structured film have been followed with spatially resolved XPS. Further chemical and structural information has been obtained with reflection absorption infrared spectroscopy (RAIRS), friction force microscopy (FFM), contact angle measurements and X-ray reflectivity (XRR). Two different types of photo-reactive functional groups have been investigated: a benzyl thiocaynate and a phenylester. First we present thin films of silanes on SiO_x, which bear the photoreactive benzyl thiocyanate (-SCN) unit. This photoisomerizes to the corresponding isothiocyanate (-NCS). The photoisomerization can be detected by a significant shift of the S2s core level. Additionally, we can prove the change of chemical reactivity due to the illumination via a post modification with fluorinated amines introduced in gas phase. Here more fluorine could be detected with the spatially resolved XPS on the illuminated areas of the sample.[1] In the second example the SiO_x substrates are modified with photosensitive silanes of different chain length containing the phenylester group. The phenylester can undergo the Photo-Fries rearrangement upon UV illumination forming a hydroxyphenyl keton. The different chemical reactivity of these two groups is again shown with a selective post modification with, e.g., fluorinated acid chlorides. The corresponding reaction has again been followed by the appearance of the F1s signal only on the illuminated areas of the samples. Finally, results of investigations extended to patterned photo-reactive thiol-SAMs on Au(111) will be discussed.

[1] A. Lex et. al., Chem. Mater. 2008, 20, 2009-2015.

9:00am **BO+SS+AS-FrM3 Odd-Even Efect in Molecular Packing and Stability of ω-Biphenyl-Alkane-Selenol SAMs on Au(111)**, ***P. Cyganik***, *K. Szelagowska-Kunstman,* Jagiellonian University, Poland, *M. Zharnikov,* Universität Heidelberg, Germany, *A. Terfort*, Marburg University, Germany

To fabricate aromatic self-assembled monolayers (SAMs) of practical importance for molecular electronics and other applications, high level of control over the SAMs properties should be achieved. In particular, besides monitoring the electronic properties, control of structure, i.e., crystallinity and defects, is an issue of equal importance. Our experimental approach to gain a general concept for the rational design of high-quality SAMs includes a systematic modification of the chemical composition of the SAM constituents and detailed investigation of the structure of the resulting films. Following this general idea, we studied the influence of the substitution of the headgroup atom (S versus Se, which binds SAMs constituent to the substrate) on the microscopic structure of hybrid aromatic-aliphatic SAMs formed on Au(111). The talk focuses on STM experiments[1] performed for the homologue series of BPnSe (CH_3-(C_6H_4)$_2$-(CH_2)$_n$-Se-, n =2-6) molecules. Obtained data are discussed and analysed in view of the spectroscopic results reported by us recently for these systems[2,3], as well as compared to the previously reported STM data[4,5] for the corresponding thiol-based analogues, i.e. BPnS/Au(111) . The main conclusions are: (1) higher structural quality of the Se based SAMs, (2) drastic changes in the BPnSe film structure depending on either odd or even value of the parameter n, accompanied by (3) the respective odd-even changes in their thermal stability.

[1] P. Cyganik et al. J. Phys. Chem. C, submited.
[2] A. Shaporenko et al. 2007 J. Am. Chem. Soc. 129, 2232.
[3] T. Weidner et al., J. Phys. Chem. C, submited.
[4] P. Cyganik et al. 2006 J. Am. Chem. Soc. 128, 13868.
[5] P. Cyganik et al. 2007 J. Phys. Chem. C. 111, 16909. .

9:20am **BO+SS+AS-FrM4 The Molecular Structure and Orientation of Phenylboronic Acid Derivatives and the Interaction with Dopamine: A NEXAFS, XPS and SPR Study**, ***C. Vahlberg***, *L. Johansson, K. Uvdal*, Linkoping University, Sweden

Our aim is to design well organized self-assembled monolayers as model systems for biological recognition such as the selective ligand - receptor interaction. These systems are important for future applications within nanoscience and the development of specific biosensors. A phenylboronic ester and a phenylboronic acid are used for surface functionalisation. Both are linked to an alkanethiol through the formation of an amide bond. Formation of a self-assembled monolayer on gold surfaces is done by common thiol chemistry. The molecular orientation and chemical composition of the two molecular systems were investigated using X-ray Photoelectron Spectroscopy (XPS), Infrared Reflection Absorption Spectroscopy (IRAS) and Near Edge X-ray Absorption Fine Structures (NEXAFS). IRAS and NEXAFS measurements showed that the two molecular systems form a well organized monolayer. The average tilt of the aromatic ring and the main molecular axis has been estimated based on NEXAFS measurements. The thicknesses of the self-assembled monolayer of the two molecules were investigated with ellipsometry and supported with XPS based measurements. The properties of the functionalized surfaces were also investigated using contact angle goniometry. Boronic acid based SAM is a simple mimicry of an adrenergic receptor. Investigation of the neurotransmitter dopamine recognition in real-time, using Surface Plasmon Resonance (SPR), is in progress.

9:40am **BO+SS+AS-FrM5 Unravelling Molecular Mechanism of Electron-Induced Cross-Linking in Aromatic SAMs**, ***A. Turchanin***, University of Bielefeld, Germany, *D. Käfer,* Ruhr-University Bochum, Germany, *M. El-Desawy,* University of Bielefeld, Germany, *Ch. Wöll, G. Witte,* Ruhr-University Bochum, Germany, *A. Gölzhäuser*, University of Bielefeld, Germany

Irradiation of aromatic self-assembled monolayers (SAMs) with low energy electrons[1] or UV-light[2] results in a lateral cross-linking and the formation of aromatic carbon nanosheets with a thickness of only one molecule. These films possess a high mechanical stability that allows their separation from the substrate and fabrication of free standing membranes with a thickness of ~1nm[3] and exhibit further a remarkable thermal stability[4] sustaining temperatures above 1000 K. Because of the promising potential of these ultrathin membranes for various applications in nano-devices, the knowledge of their molecular microstructure and the mechanisms of cross-linking are of great interest. We have employed a variety of in situ spectroscopic techniques including X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure spectroscopy (NEXAFS), thermal desorption spectroscopy (TDS), and UV photoelectron spectroscopy (UPS) to characterize the electron irradiation of 1,1'-biphenyl-4-thiol (BPT) SAMs on Au. Experimental data are further compared with quantum chemical calculations of the electronic structure of cross-linked species, which allowed the identification of distinct molecular species leading to the formation of carbon nanosheets upon electron irradiation of BPT SAMs. Molecular mechanisms of the electron induced changes in aromatic SAMs will be discussed.

[1]Geyer, W.; Stadler, V.; Eck, W.; Zharnikov, M.; Gölzhäuser, A.; Grunze, M.; Appl. Phys. Lett. 75 (1999) 2401;
[2]Turchanin, A.; Schnietz, M.; El-Desawy, M.; Solak, H. H.; David, C.; Gölzhäuser, A.; Small 3 (2007) 2114.;
[3]Eck, W.; Küller, A.; Grunze, M.; Völkel, B.; Gölzhäuser, A.; Adv. Mater. 17 (2005) 2583.;
[4]Turchanin, A.; El-Desawy, M.; Gölzhäuser, A.; Appl. Phys. Lett. 90 (2007) 053102.

10:00am **BO+SS+AS-FrM6 Surface-Active Catechol Derivatives on Metal Oxide Surfaces: Influence of Molecular Architecture and Conditions on Polymer Adlayer Formations and Stability**, ***B. Malisova***, ETH Zurich, Switzerland, *K. Gademann,* EPFL Lausanne, Switzerland, *S. Zuercher, S. Tosatti, M. Textor*, ETH Zurich, Switzerland

In recent works, L-3,4-dihydroxyphenylalanine (DOPA), a catechol which is found in mussel adhesive proteins (MAPs), served as basis for poly(ethylene glycol) (PEG) ultra thin coatings capable of rendering surfaces non-fouling,[1] i.e. resistant to non-specific protein adsorption and capable of withstand formation of biofilm by microorganisms.[2] However, it was found that the negative charge of DOPA at physiological pH where most metal oxide surfaces are negatively charged reduces adsorption due to electrostatic repulsion effects unless at least three residues per PEG chain are used.[3] We have been able to overcome this problem by synthesizing a

new positively charged catechol derivative (anacat)[4] based on the iron chelator anachelin which was evolutionarily developed by cyanobacteria to bind Fe(III). Incorporation of an additional positive charge resulted in a stable, protein-resistant, non-fouling coating of TiO_2.[5] In order to further study the effect of the charge of binding groups on the adlayer formation process as well as the effect of acidity of catecholic –OH groups, 5 different catechol binding feet were synthesized and coupled to PEG chains. Adsorption and stability properties together with the abilities to resist protein adsorption are analyzed as function of different adsorption parameters (pH, substrate type, salt concentration and temperature) by Ellipsometry (ELM) and X-Ray Photoelectron Spectroscopy (XPS). Current results suggest that the charge of the binding group, which should be opposite to the one of the substrate, as well as the difference between adsorption pH and the isoelectric point of the substrate are important parameters for all investigated molecules. Final goal of the present work is the development of a general model that explains the binding mechanism of catechols onto metal oxide substrates as function of the binding group acidity.

[1] Gunawan, R. et al. Langmuir 2007, 23, (21), 10635-10643.
[2] Hall-Stoodley, L. et al. Nature Reviews Microbiology 2004, 2, (2), 95-108.
[3] Dalsin, J. et al. Langmuir 2005, 21, (2), 640-646.
[4] Gademann, K. et al. Angew. Chem. Int. Ed. 2004, 43, (25), 3327-3329.
[5] Zurcher, S. et al. JACS 2006, 128, (4), 1064-1065.

10:20am **BO+SS+AS-FrM7 Self-Assembly of Methanethiol on the Reconstructed Au(111) Surface**, ***G. Nenchev***, *B. Diaconescu*, University of New Hampshire, *F. Hagelberg*, East Tennessee State University, *K. Pohl*, University of New Hampshire

The molecular self-assembly of alkanethiols ($CH_3(CH_2)_{n-1}SH$) on Au(111) surface has been studied extensively in the last 20 years. Despite the abundance of experimental and theoretical data, the true nature of the processes involved in the monolayer formation is still not fully established. We will present a combined UHV VT-STM and DFT study of the adsorption of the simplest alkanethiol, methanethiol (CH_3SH), on the reconstructed Au(111) surface. Our findings challenge the established notion that methanethiol is too short to form ordered structures even at low temperature. At sub-monolayer coverage, dimer chains are resolved on the FCC areas of the reconstruction pattern. At higher coverage the monolayer evolves into two continuous self-assembled phases: a rectangular c($4\sqrt{3}$ x 2) phase, which coexists with the substrate reconstruction network, and a close-packed p($\sqrt{3}$ x $\sqrt{3}$)R30° hexagonal phase. Our DFT calculation, which takes the reconstruction of the surface into account, confirms the non-dissociative character of the methanethiol adsorption and derives the bonding geometry of the molecular dimers - a sequence of shifted hollow-top and hollow-bridge bonding positions. The numerical calculation reveals that, in stark contrast to longer alkanethiols, at low temperature the self-assembly process of methanethiol is not driven by Van der Waals forces, but by a surface-mediated interaction. These novel results clearly demonstrate the unique nature of the methanethiol adsorption and self-assembly.

This work is supported by the National Science Foundation under Award #0425826 for the Center for High-Rate Nanomanufacturing and under Grant No. DMR-0134933. The computations are performed on the CRAY XT3 machine Sapphire at US Army/Engineer Research and Development Center (ERDC, Vicksburg, MS) in collaboration with Jackson State University, and supported by the DoD through Contract #W912HZ-06-C-005.

10:40am **BO+SS+AS-FrM8 Thermo Scientific Theta Probe : Measuring the Quality of Self-Assembled Monlayers on Gold**, ***P. Mack***, Thermo Fisher Scientific, UK, *D.J. Graham*, Asemblon Inc, *J. Wolstenholme*, *R.G. White*, Thermo Fisher Scientific, UK

Self assembled monolayers (SAMs) are becoming increasingly important as a means to functionalise surfaces and to control surface properties or reactivity. The attributes of angle resolved X-ray photoelectron spectroscopy (ARXPS), such as surface specificity, chemical selectivity and non-destructive depth profiling, make it the ideal technique for characterising these layers. The Thermo Scientific Theta Probe was used to characterise the quality of self assembled monolayers on gold surfaces. For alkanethiol layers with high coverage, bonding was almost entirely via the thiol group (forming Au-S bonds). Mixed bonding modes were observed, however, with lower coverage, in agreement with a proposed mechanism for the formation of these films. The influence of the head group of the self-assembly precursor was investigated by analysing hydroxyalkanethiol and ethylene glycol monolayers.

11:00am **BO+SS+AS-FrM9 Morphology and Bonding in Alkene and Alkyne Based Monolayers Chemomechanically Formed on Si Surfaces**, ***T.M. Willey***, Lawrence Livermore National Laboratory, *M.V. Lee*, Materials Nanoarchitectonics, Japan, *J.R.I. Lee*, Lawrence Livermore National Laboratory, *M.R. Linford*, Brigham Young University

One of the most simple and economical methods for attaching and patterning alkenes or alkynes on silicon surfaces is through chemomechanical modification. Scribing the Si removes the oxide passivation layer, allowing the alkene or alkyne to chemisorb to the exposed and highly reactive Si surface. Near-edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy reveals chemically homogeneous films with nearly monolayer coverage. Both alkene and alkyne precursors show no orientational order; however, more rigid perfluoronated molecules do have some incident angle dependence in NEXAFS resonances. Both alkenes and alkynes retain significant sp/sp^2 content. Hypothesized mechanisms of chemisorption are presented based on comparing the intensity of the sp/sp^2 features in the NEXAFS acquired from monolayers to measurements of precursor alkenes and alkynes in the gas-phase.

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