Thursday Morning, October 28, 1999

Surface Science Division Room 606 - Session SS1+AS+BI-ThM

Self-Assembled Monolayers

Moderator: N.D. Shinn, Sandia National Laboratories

8:20am SS1+AS+BI-ThM1 Two-Dimensional Phase Transitions in Amphiphile Monolayers, G.E. Poirier, National Institute of Standards and Technology

Recently scientists have explored methods of constructing complex chemically patterned surfaces with the goal of making novel biosensors or of realizing lab-on-a-chip technology. In order to design patterned monolayers it is important to understand how these molecules behave in two dimensions, what is the molecular packing of the surface phases and which phases coexist in thermodynamic equilibrium. The goal of this presentation is to describe the two-dimensional structural phases of decanethiol monolayers. Our studies were conducted using gas-phase transport of decanethiol onto clean Au(111) in an ultrahigh vacuum scanning tunneling microscope. With increasing surface coverage, the monolayer sequentially adopts six discrete structural phases. At low surface coverage, decanethiol exists as a lattice gas. With increasing coverage the molecules sequentially condense into islands of three discrete commensurate crystalline lattices, each characterized by alignment of the molecular axes with the surface plane, but with discretely increasing degrees of out-of-plane interdigitation. Above saturation coverage of the densest surface-aligned phase, the monolayer undergoes an edgemediated melting transition. The c(3x2/3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleates and grows from this liquid. These studies provided a detailed, real-space picture of the coverage-dependent phases and phase transitions of alkanethiol molecular monolayers on Au(111).

8:40am SS1+AS+BI-ThM2 Surface Phase Transitions of Asymmetric Dialkyl Disulfide Self-Assembled Monolayers, *M. Hara*, *K. Kamei*, *T. Araki*, *K. Fujita*, *W. Knoll*, Frontier Research Program, RIKEN, Japan

Adsorption and desorption processes of asymmetric dialkyl disulfide (hexyl octadecyl disulfide: C6-SS-C18) self-assembled monolayers (SAMs) on Au(111) have been investigated by surface plasmon resonance (SPR), mass spectroscopy (MS), thermal desorption spectroscopy (TDS), and scanning tunneling microscopy (STM). Formation of C6-SS-C6 and C18-SS-C18 dimer species in the monolayer and also in the solution through dimerization and exchange processes has been confirmed during the monolayer growth. In the TDS spectra for shorter immersion SAMs, C6 monomer species showed the strong peaks, and gradually C6-SS-C6 dimer and C18 monomer peaks become stronger for longer immersion. Phase-separated domains of pure C6 and pure C18 striped phases have been visualized in the initial growth stage by STM and the area of the C6 domain was larger than that of C18 one. These results suggest that S-S bonds were cleaved when disulfides adsorbed on Au surface followed by the surface diffusion to form phase separation before standing-up SAM formation. After the C6-rich SAM growth, molecules are dimerized and then exchange process starts from the weakly bound C6-SS-C6 dimers toward C18-rich SAM. SPR kinetics studies also showed the double exponential growth which is different from usual Langmuir adsorption isotherm. Following those results, we propose more detailed surface phase transition model of alkanethiol SAM growth through the dimerization and the exchange processes.

9:00am SS1+AS+BI-ThM3 Structure, Bonding and Reactivity of Selfassembled Monolayers, G.J. Leggett, B.D. Beake, N.D. Brewer, UMIST, UK; E. Cooper, Glaxo-Wellcome, UK; D.A. Hutt, University of Loughborough, UK Two approaches to the characterisation of the nature of the sulfur bonding environment in self-assembled monolayers (SAMs) have been explored: sulfur K-edge surface extended X-ray absorption fine structure (SEXAFS) and static secondary ion mass spectrometry (SIMS). S K-edge SEXAFS has proved highly effective for SAMs on Ag and has confirmed that the sulfur adsorbs with threefold coordination during both solution-phase adsorption onto polycrystalline Ag and gas-phase adsorption onto Ag(111) single crystal surfaces. There is no change in the S adsorption site with coverage. Static SIMS has yielded powerful insights into the effect of electron beam bombardment on SAM structure. A complete loss of all gold-molecular fragments from the spectrum is observed after small doses of electrons, indicating a rapid alteration of the sulfur bonding environment, due either to S-C bond scission or, more likely, to oxidation of thiolates to disulfides. Changes in Au-S bonding during the formation of the low coverage phase

of butanethiol on Au have also been studied by static SIMS. Photo- and airoxidation rates are influenced by the adsorbate alkyl chain length; rates of both processes decrease with increasing chain length due to increasing SAM ordering. The nature of the terminal group also affects rates of oxidation, and has a profound influence on the stability of the SAM. Hydrogen bonding between neighbouring terminal groups leads to significant stabilisation. Friction coefficients may be measured for SAMs using friction force microscopy. These decrease with increasing alkyl chain length, and are higher for adsorbates with polar terminal groups. Oxidation of methyl terminated SAMs leads to an increase in the coefficient of friction, interpreted in terms of the collapse of film order following head group oxidation. The rate of increase in the coefficient of friction is faster for short chain SAMs than long-chain SAMs, in agreement with the findings of static SIMS studies.

9:20am SS1+AS+BI-ThM4 Structure of Partially Fluorinated n-alkanethiols on Polycrystalline Gold and Silver Surfaces, *S. Frey*, Universität Heidelberg, Germany; *K. Tamada*, National Institute of Materials and Chemical Research, Japan; *K. Heister, M. Zharnikov, M. Grunze*, Universität Heidelberg, Germany

The physical and chemical properties of self-assembled monolayers (SAM) of alkanethiols (AT) are noticeably affected by partial fluorination of the hydrocarbon chain. We have studied the structure of SAMs formed from partially fluorinated alkanethiols (PFAT) CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub n@SH with different hydrocarbon chain length (n = 2, 11 and 17) on Au and Ag coated silicon wafers. The objectives of our experiments were (i) to find out whether PFAT form ordered and densely packed SAMs on these substrates, (ii) to determine the individual conformation and orientation of the hydro- and fluorocarbon parts in the molecules, and (iii) to clarify the influence of the headgroup-metal bond (RS-Au or RS-Ag) on the film structure. The PFAT films were characterized by atomic force microscopy, infrared reflection absorption spectroscopy, Xray photoelectron spectroscopy, and angle resolved near edge X-ray absorption fine structure spectroscopy. PFATs were found to form highly ordered and densely packed SAMs on polycrystalline Au and Ag. The hydrocarbon and fluorocarbon chains of the adsorbed PFATs retain the expected planar zigzag and helical conformation of the bulk materials, respectively. The fluorocarbon chains, which are oriented almost perpendicular to the substrates for CF@sub 3@(CF@sub 2@)@sub 9@(CH@sub 2@)@sub 2@SH, assume a more tilted orientation in PFAT SAMs with longer hydrocarbon moieties. As found for the AT on Ag and Au. the hydrocarbon part in the PFAT films exhibits smaller tilt and twist angles on Ag as compared to the Au substrates. Considering the reduced van der Waals interaction between the hydrocarbon chains in PFAT as compared to neat AT SAMs (due to the sterical constraints provided by the fluorocarbon chains), the differences in tilt and twist angle appears to be associated with the different character of the headgroup-substrate bonding on Au and Ag. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft, Forschung und Technologie through grant No. 05 SF8VHA 1.

9:40am SS1+AS+BI-ThM5 Controlling the Placement of Molecules in the Self Assembly and Directed Assembly of Organic Monolayers, *P.S. Weiss, D.L. Allara, L.A. Bumm, J.J. Jackiw,* The Pennsylvania State University INVITED

We manipulate and measure the structures of monolayer films in order to tune their properties. This is accomplished by controlling the defect type and density in the films. We then process the films to insert single molecules, to insert bundles of molecules, or to graft new molecular terraces onto existing domains by using these defects to advantage. The inserted molecules can serve as the anchor points for polymerization; this allows us to choose to produce single polymer dots or isolated polymer brushes. We connect our scanning tunneling microscopy measurements to electron transfer phenomena which are ubiquitous in such areas as biochemistry and electrochemistry by separating the transconductance into components arising from transport through the molecule vs. the tunneling gap outside the film. We show how these components can be measured independently. We prepare films predicted to have many equivalent defect sites so as to provide identical matrix isolation environments for single molecular wire candidates. We also prepare films with well defined interfaces between separated components so that insertion, deposition, or reaction can be directed to these molecularly sharp boundaries.

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10:20am SS1+AS+BI-ThM7 Protein Adsorption to Model Surfaces: Probe Adhesion Between Fibrinogen and Patterned SAMs, *L.F. Pardo*, *T.B. Boland*, Clemson University

Interactions between blood and an artificial surface induce a rapid, thrombogenic response believed to be mediated by protein adsorption. In this study, atomic force microscopy (AFM) was used to measure directly non-specific forces between proteins and functionalized surfaces. A protein-modified AFM cantilever tip was used to probe of interactions between a model substrate and a single protein. Model surfaces consisted of both simple and microcontact-printed, -OH, -COOH, and -CH3 terminated self-assembled monolayers (SAMs) of alkanethiols on gold. Fibrinogen was used as the model protein due to its significance in biomaterial-mediated inflammatory responses. It was tethered to the probe tip using a synthetic polypeptide (polyserine). Various approaches were taken to link polyserine to a self-assembled monolayer on a gold substrate. Ellipsometric and vibrational spectroscopic measurements indicated that successive carbodiimide activation of a carboxyl-terminated alkanethiol and polyserine allowed for the successful formation of a polyserine-tethered fibrinogen film. The SAMs, polyserine and fibrinogen films were characterized by ellipsometry and contact angle measurements. Both AFM images and measurements will be presented and discussed. An understanding of how fibringen interacts under model conditions will give insight into more complicated real systems.

10:40am SS1+AS+BI-ThM8 Modification of Self-Assembled Monolayers by X-ray, Electron and Thermal Treatments, *H. Fairbrother*, *A. Wagner*, *K. Han*, Johns Hopkins University

Polymer surface modification strategies are widely used to modify interfacial characteristics, including permeability, wettability, adhesion, friction, wear and biocompatibilty. To better understand the detailed nature of these processes thiol-based self-assembled monolayers (SAMs) adsorbed on Au substrates have been used as models for the polymeric interface. In the case of X-ray modification results from X-ray Photoelectron Spectroscopy on fluorinated SAMs show that the degree of cross-linking can be directly correlated with the appearance of CF groups in the organic film. Additional information from Reflection Absorption Spectroscopy and Atomic Force Microscopy on the impact of X-ray, electron, and thermal modification treatments will also be presented, enabling a detailed picture of the chemical and physical modifications that occur during surface treatments to be constructed.

11:00am SS1+AS+BI-ThM9 Electron-induced Damage in Thiofunctionalized Alkanethiol Monolayers, K. Heister, W. Geyer, S. Frey, Universität Heidelberg, Germany; A. Ulman, Polytechnic University; A. Gölzhäuser, M. Zharnikov, Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) of alkanethiols (AT) as lithographic resist require an increased sensitivity of these systems toward ions, X-ray photon or electron irradiation. This effect can be achieved by incorporation of specific molecular groups associated with comparatively weak bonds, such as C-S bond provided by sulfide -Sand sulfone SO@sub 2@- moieties, in the aliphatic chains. We have investigated the damage induced by low-energy electrons in SAMs formed from C@sub 6@H@sub 13@SC@sub 11@H@sub 22@SH (I), C@sub 6@H@sub 13@SO@sub 2@C@sub 11@H@sub 22@SH (II), C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 12@SH (III), and C@sub 11@H@sub 23@SO@sub 2@C@sub 6@H@sub 4@OC@sub 5@H@sub 10@SH (IV) on polycrystalline Au substrates using angle-resolved near edge X-ray absorption fine structure spectroscopy and X-ray photoelectron spectroscopy. Similar to AT SAMs, an irradiation-induced disordering and a dehydrogenation of the pristine films I - IV as well as the desorption of molecule fragments and the transformation of thiolate moieties in a new irradiation-induced sulfur species were observed. The extent of the irradiation-induced events is, however, affected by the introduction of the sulfide and sulfone moieties. An increased extent of the irradiation-induced desorption processes as compared to AT SAMs was found in I and II, which implies that bond scission events predominately occur in the outermost part of AT SAM. Controversially, an additional dipolar interchain interaction provided by the sulfonic entities has a stabilizing influence on the lower part of SAMs II-IV leading to the conservation of the pristine thiolate species responsible for anchoring of the alkyl chains to the substrate. Considering these controversial effects provided by the sulfonic groups the incorporation of sulfide moiety seems to be a better choice to improve the sensitivity of AT SAMs toward electron irradiation.

11:20am SS1+AS+BI-ThM10 Sensitivity of Alkanethiol Self-assembled Monolayers toward Low-energy Electron Irradiation, *M. Zharnikov, S. Frey, K. Heister, M. Grunze*, Universität Heidelberg, Germany

Potential technological applications of self-assembled monolayers (SAM) as lithographic resist involve their exposure to jons. X-ray photons or electrons. We have investigated the damage induced by low-energy electrons in SAMs of dodecanethiolate (DDT), octadecanethiolate (ODT) and perdeuterated eicosanethiolate (PDET) on gold and of ODT on silver using x-ray photoelectron spectroscopy and angle resolved near edge x-ray absorption fine structure spectroscopy. ODT/Au was taken as a reference system, whereas the other SAMs differed from ODT/Au in the length (DDT/Au) and the isotopic composition (PDET/Au) of the alkyl chains and the strength and character of the thiolate-metal bond (ODT/Ag). All systems studied were found to exhibit a qualitatively similar behavior with respect to low-energy electron irradiation. Both the alkyl chains and the S-Au interface are affected simultaneously through the electron-induced dissociation of C-H, C-C, C-S, and metal-thiolate bonds. The most noticeable processes are the loss of the orientational and conformational order. partial dehydrogenation with C=C double bond formation, desorption of film fragments, decrease of thiolate species, and the appearance of new sulfur species. The cross sections for the individual irradiation-induced processes have been determined. The reactions of the alkyl matrix and the S-metal interface to electron irradiation are essentially independent. The extent and rate of thiolate species reduction and new sulfur species formation are mainly determined by the strength and character of the thiolate-metal bond (Au vs. Ag). At the same time, an extent of irradiationinduced desorption of sulfur-containing fragments depends on the alkyl chain length. Only a slight isotopic variation in the irradiation-induced dehydrogenated process was observed.

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