

Wednesday Morning, November 4, 1998

Applied Surface Science Division Room 307 - Session AS+BI+SS-WeM

Organized Molecular Monolayers

Moderator: H.G. Tompkins, Motorola, Inc.

8:20am **AS+BI+SS-WeM1 Structural Characterization of the Outermost Surface Monolayers of CH@sub 3@ and CF@sub 3@ Terminated n-Alkanethiol Monolayers Self-Assembled on Au(111)**, L. Houssiau, J.W. Rabalais, University of Houston

Time-of-flight scattering and recoiling spectrometry (TOF-SARS) was used for surface elemental and structural characterization of hexa- and heptadecanethiols (C@sub 16@ and C@sub 17@ for short) and of 16,16,16-trifluorohexadecanethiol (FC@sub 16@) self-assembled monolayers (SAMs) on a Au(111) surface. The substrate was also characterized after in-situ sputtering and annealing by TOF-SARS and LEED in order to identify its crystalline orientation. The azimuthal angle scans performed on the C@sub 16@ samples displayed unique features, indicating well-ordered structures. The recoiling intensities of the H and C atoms exhibited a clear 60° periodicity, with H recoil maxima and C recoil minima displayed at 30° from the substrate nearest-neighbor directions. Several models were tested by means of classical ion trajectory simulations using the scattering and recoiling imaging code (SARIC). The molecular length, tilt angle, and twist angle were varied in the simulations. Good agreement between the experiments and simulations for both C and H signals was obtained for a (@sr@3x@sr@3)R30 structure of SAM lattice, with the molecules tilted along the substrate nearest-neighbor directions by 35° from the surface normal. Moreover, a twisting of the molecular plane by 55° from the plane normal to the surface had to be considered in order to reproduce the H angular variations. Similar measurements on the C@sub 17@ samples showed much weaker variations for the H and C recoil intensities. This is believed to be due to the high tilt angle of the end methyl group. The FC@sub 16@ samples showed the presence of C and F atoms in the surface layer. No evidence for H and C recoil azimuthal variation was observed on the FC@sub 16@ samples, although a weak azimuthal periodicity was noticed for the F recoils.

8:40am **AS+BI+SS-WeM2 Fundamental Studies of Phase Transitions in Functionalized Amphiphile Monolayers**, G.E. Poirier, National Institute of Standards and Technology

Alkanethiol molecules chemisorb strongly to noble metal surfaces. Intermolecular dispersion forces compress the molecules into a dense, commensurate, crystalline film that spontaneously terminates growth at one molecular monolayer. The thickness of the film, its dielectric constant, and the physical properties of the exposed surface can be controlled by changing the length of the alkyl chain, its degree of saturation, and its terminal functional group, respectively. These systems are therefore desirable in any application requiring control of the adhesive, tribological, or electron transfer properties of metal surfaces. This talk will outline experiments in which methyl-terminated alkanethiol monolayers were prepared by vapor deposition onto clean Au(111) in ultra-high vacuum and characterized in-situ using molecular-resolution scanning tunneling microscopy.

9:00am **AS+BI+SS-WeM3 Characterization of Fluorinated Monolayers**, D.G. Castner, University of Washington

INVITED

Self assembly processes have made it possible to prepare organic monolayers with well-defined surface structures and chemistries. The ability to systematically vary the surface structure and chemistry of these self-assembled monolayers (SAMs) provide an excellent method for examining the relationship between the surface properties of a film and its performance in a given application (e.g., cell culture). To develop these relationships requires detailed characterization of the surface composition, molecular structure, orientation, and topography of the films with techniques such as XPS, ToF SIMS, NEXAFS, and STM. How the methods and molecules used to form fluorinated films affect the resulting film structure will be discussed. The degree of ordering and relative orientation in SAMs prepared with perfluoroalkyl thiols depend on the length of the fluorinated tail. Although SAMs prepared from thiols with long perfluoroalkyl tails are highly ordered, their stability is limited by the single point attachment of the Au-S bond. This stability can be increased by using grafted copolymers containing both perfluorinated and alkanethiol side chains to generate multipoint attachment of each polymer chain. However, this method of increasing film stability also results in a decreased degree of film orientation. Typically films prepared using polymers with perfluorinated side chains are highly disordered. Only at high

concentrations of perfluoroalkyl side chains (>50%) is any ordering detected in polymeric monolayers. Other methods, such as trifluoroacetic anhydride derivatization of hydroxyl-terminated alkanethiols can also be used to produce fluorinated surfaces. Depending on the derivatization system, the high degree of ordering in the starting SAM can be retained after derivatization.

9:40am **AS+BI+SS-WeM5 Controlling Defects in Self-Assembled Monolayers**, J.J. Jackiw, J.J. Arnold, J.A. Johnson, T.D. Dunbar, T.L. Spiva, D.L. Allara, P.S. Weiss, The Pennsylvania State University

Much is known about the formation, structure, stability, and properties of alkanethiolate monolayers on Au (111). We have begun to explore the effects of changing the molecule-surface linkage. In the cases of alkanethiolates and alkaneselenolates, monolayers can be made respectively from: thiols and selenols, disulfides and diselenides, and by deprotecting alkanethioacetates and alkaneselenoacetates, which are less prone to oxidation. Our experiments probe monolayer structures and defects resulting from the deposition of dodecanethiol, didodecane disulfide, didodecane diselenide, dodecaneselenol, and in situ deprotected dodecanethioacetate and dodecaneselenoacetate. We compare the structures and defects in the resulting monolayers. The defect identities and densities are important in determining the properties of the films, especially our ability to manipulate their structures and compositions.

10:00am **AS+BI+SS-WeM6 New Preparation Methods for Self Assembly of Alkanethiolates on III-V Semiconductor Surfaces**, C.K. Mars, D.L. Allara, Pennsylvania State University

The ability to control the chemical composition of III-V surfaces is vital in semiconductor technology. Alkanethiolate monolayers prepared from thiol melts at temperatures near 100°C have been shown to mimic the improved electronic passivation properties seen on III-V semiconductors with Na@sub 2@S and NH@sub 4@S@sub x@ treatments. We have developed a new process by which these films can be grown reliably in a highly organized state from millimolar ethanol solutions near 50°C. In addition, by adding controlled amounts of base to these solutions, the degree of organization as determined by IR spectroscopy and contact angle measurements, can further be improved. This new process has allowed us to deposit a wide variety of films including aromatic and functionalized molecules as well as layers anchored by other chalcogenide elements.

10:20am **AS+BI+SS-WeM7 The Effect of Solvents and Electrical Fields on the Molecular Conformation in Organic Monolayers**, M. Grunze, M. Buck, F. Eisert, M. Zolk, P. Harder, University of Heidelberg, Germany; A. Pertsin, Russian Academy of Sciences, Russia; H.J. Kreuzer, Dalhousie University, Canada

INVITED

The molecular conformation in self-assembled monolayers (SAMs) of functionalized alkanethiols is affected by the presence of solvents. The polarity and ability of the solvent molecules to form hydrogen bridge bonds, and the lateral density in the SAMs determines the orientation of the terminal functional moiety at the organic film/solvent interface. We will discuss our in situ Sum Frequency Generation (SFG) and protein adsorption experiments on methyl- and oligo(ethylene glycol)-terminated self-assembled alkanethiolate monolayers, and present atomistic force field calculations to explain our data. These results show that spectroscopic measurements taken in vacuum or ambient atmosphere are not necessarily representative for the molecular structure and chemical nature of organic surfaces immersed in a liquid.

11:00am **AS+BI+SS-WeM9 Nanometer-Scale Design and Fabrication of Polymer Interfaces using Polydiacetylene Monolayers**, M.D. Mowery¹, M. Cai, University of Michigan; H. Menzel, University of Hannover, Germany; C.E. Evans, University of Michigan

The selective control of polymer interfacial characteristics such as viscoelasticity and electronic properties is crucial for numerous important applications from sensor design to device fabrication. In this work, robust interfacial polymer films are successfully fabricated within a single molecular layer with nanometer-scale control of the polymer physical structure. The formation of these unique polymer films is accomplished by the spontaneous assembly of alkyl disulfide precursors containing conjugated diacetylene groups at the gold-solution interface. The resultant well-defined monomer assembly is covalently linked through UV photopolymerization, forming a highly conjugated polymer backbone parallel to the surface. Nanometer-scale control of the interfacial structure is accomplished by manipulating the vertical position of the polymer

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backbone within the single layer assembly. Additionally, photo-templating affords lateral control over the formation of polymer domains. These subtle variations in physical structure have a profound impact on the global electronic and viscoelastic properties of the polymer interface. The impact of these structural variations is demonstrated by surface infrared and Raman spectroscopy as well as electrochemical capacitance, heterogeneous electron transfer, and reductive desorption measurements. Furthermore, AFM is utilized to physically image the interfacial structure and evaluate the polymer viscoelastic properties. Finally, the application of these monolayer polymers for lithographic applications and the implications for interfacial design are discussed.

11:20am **AS+BI+SS-WeM10 Bias-dependent Contrast in STM Images of Phenyl octadecylethers**, *I.H. Musselman, H.S. Lee, S. Iyengar*, University of Texas, Dallas

A homologous series of para-substituted phenyl octadecylethers (X-POEs, X = H, Cl, Br and I) was prepared and characterized using ^1H NMR and GC/MS. Scanning tunneling microscopy (STM) images were acquired from monolayers of the ethers physisorbed onto highly oriented pyrolytic graphite. The contrast exhibited by the X-POE molecules in these images varied as a function of tip-sample bias. For example, STM images acquired at biases of approximately -0.5 to -0.6 V (sample negative) exhibited a dim alkyl tail and a series of bright spots corresponding to functionalities in the head group (e.g. halogen, phenyl group, oxygen). However, at biases more negative than -1.2 V, the largest contribution to contrast was observed for the alkyl tail (e.g. octadecyl group). A comparison of STM images of the adsorbed X-POE molecules with electron density contours calculated using HyperChem suggested a bias-dependent participation of individual bonding molecular orbitals to tunneling. A resonance tunneling mechanism between the tip and molecular orbitals adjacent to and including the highest occupied molecular orbital (HOMO) is proposed. ¹ The support of this research by a grant from the Robert A. Welch Foundation is gratefully acknowledged.

11:40am **AS+BI+SS-WeM11 Self-Assembling Trichloro- and Trimethoxysilanes on TiO₂(100) Crystal**, *R. Magnée, J.-J. Pireaux*, LISE - Facultés Universitaires Notre-Dame de la Paix, Belgium

Trichlorosilanes ($\text{CH}_3(\text{CH}_2)_n\text{SiCl}_3$, $n = 1, 7, 17$) and trimethoxysilanes ($\text{CH}_3(\text{CH}_2)_n\text{Si}(\text{OCH}_3)_3$, $n = 2, 7, 17$) SAM's were deposited by dipping a TiO₂(100) crystal in a 10^{-3} M toluene solution for 4 hours. The titanium dioxide surface was prepared by Ar⁺ sputtering, annealing in UHV to get a clear LEED (1x3) pattern, then exposed to atmosphere before dipping. Silane molecules need H₂O or a hydroxylated surface to react but it was not necessary to hydroxylate the TiO₂ because of the air exposure. Hydroxylation was confirmed by FT-IR and XPS. X-Ray and Ultra-violet Photoelectrons Spectroscopy (XPS, UPS) were then used for the SAM's characterization. We expect a siloxane network to appear at the interface in addition to the Ti-O-Si bonds. XPS results show that the silane groups do indeed bind to the TiO₂ surface but that some defects are also present at the interface: for $n=17$ the amount of OH groups is 4 % of the total oxygen signal while this value is doubled for $n=7$. Probably due to the higher reactivity of chlorine atoms, trichlorosilanes present less defects than trimethoxysilanes. By comparison with theoretical calculations,¹ UPS provides information on the alkane chain conformation: we show that longer silane molecules ($n=17$) are grafted in a zigzag planar conformation, while $n=7$ molecules seem to present chain defects. This is consistent with the self-assembling process that depends on long-range interchain interactions. For the smallest chains ($n=1,2$), the XPS C/Si ratios are always too high, suggesting some contamination: this is probably due to solvent incorporation in the layer. HREELS analysis (not yet performed at the date of abstract submission) may help to get more information on the order of the layers. ¹ A.-S. Duwez, S. Di Paolo, J. Ghijsen, J. Riga, M. Deleuze, J. Delhalle, J. Phys. Chem. B, 101 (1997) 884.

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