

Surface Science

Room 202 - Session SS+EM-WeM

Self-Assembled Monolayers

Moderator: P.S. Weiss, The Pennsylvania State University

8:20am **SS+EM-WeM1 Investigation of Mixed Fluorocarbon/Hydrocarbon Self-Assembled Monolayers on Au by Reactive Ion Scattering Spectrometry**, X. Yang, University of Arizona; S. Ravindran, University of Texas; A. Graham, K. Nebesny, University of Arizona; T.R. Lee, University of Houston; N.R. Armstrong, V.H. Wysocki, University of Arizona

A series of mixed self-assembled monolayers (SAMs) of CF@sub 3@CF@sub 2@(CH@sub 2@)@sub 14@SH (C16F2) and CH@sub 3@(CH@sub 2@)@sub 15@SH (C16) were prepared on polycrystalline gold. Surface composition and crystallinity were first examined by XPS, FT-RAIRS and contact angle. Homogeneously mixed and well-ordered surfaces were formed. Results showed that surface composition followed solution composition uniformly. Reactive Ion Scattering Spectrometry (RISS) utilizing low-energy (<100eV) ion-surface collisions was used to investigate the mixture monolayers. Experiments are carried out in a tandem quadrupole mass spectrometer. Precursor ions selected by the first quadrupole collide onto the surfaces at given collision energies. Neutralization and fragmentation of projectiles, ion-surface reaction and sputtering of surface species occur upon collision of the projectile ions with the surface. Product ions are extracted and analyzed by the second quadrupole. Benzene, tungsten hexacarbonyl and d4-pyrazine positive radical ions were used as projectile ions. As C16F2 concentration increases on the surface, projectile neutralization decreases, the amount of methyl/hydrogen abstraction decreases non-linearly, and linear increases of translational to internal energy conversion upon collision of either benzene or tungsten hexacarbonyl are shown. RISS shows high sensitivity to composition and homogeneity of surfaces.

8:40am **SS+EM-WeM2 Surface Bonding and Dynamical Behavior of CH@sub 3@SH on Au(111)**, P. Maksymovych, University of Pittsburgh; D.C. Sorescu, U.S. Department of Energy; D.B. Dougherty, J.T. Yates, Jr., University of Pittsburgh

Alkanethiols are often used for the growth of self-assembled monolayers, which are ordered 2-D molecular films covalently bonded to a substrate, typically a gold surface. The bonding of alkanethiols to gold has remained a controversial issue. In particular, the bonding of the undissociated alkanethiols has not been addressed at the atomic scale so far. We have studied adsorption and surface chemistry of the smallest alkanethiol, CH@sub 3@SH, on the Au(111) surface using the Scanning Tunneling Microscopy (STM) at 5K and Density Functional Theory (DFT). It has been established that CH@sub 3@SH adsorbs and desorbs without dissociation. Using the STM, it was found that CH@sub 3@SH adsorbs on top of an Au atom on the defect-free surface, and undergoes hindered rotation at 5K. The barrier to rotation obtained by DFT calculations is ~0.1 kcal*mol@super -@@super 1@. The STM image of the rotating molecule has a shape of a flower with six petals. The pattern suggests that the potential minima directions occur for the rotating molecule at the six hollow sites surrounding the atop adsorption site. Furthermore, selective site occupation was observed on the length-scale of the herringbone reconstruction of the Au(111) surface. At very low coverage, the CH@sub 3@SH molecule was found to preferentially adsorb on the intrinsic defective sites on the surface, such as the herringbone "elbows" and random atomic step sites. At higher coverage preferential adsorption occurred on the fcc-stacked regions of the herringbone reconstruction. The latter is explained by the variation of the surface stress across the Au(111) surface due to the herringbone reconstruction, which causes the mobile CH@sub 3@SH molecules to select the most exothermic adsorption sites available at various coverages. We thank the W. M. Keck Foundation and NEDO (Japan) for financial support of this work.

9:00am **SS+EM-WeM3 Diffusion and Aggregation of Thiol-Linked Organic Molecules on a Cu(111) Surface**, K.L. Wong, K.-Y. Kwon, X. Lin, L. Bartels, University of California at Riverside

We have investigated the adsorption geometry and the detailed surface dynamic behavior of benzenethiol (BT) molecules on a Cu(111) surface at low temperatures (50-60K). We chose BT as a model system, because it contains both the aromatic moiety and the thiol linker common in melectronic molecules, yet it is sufficiently small to be treated at high resolution experimentally and theoretically. The BT molecule adsorbs onto

Cu(111) in two types of adsorption sites. In both cases the sulphur atom is believed to be adsorbed near the fcc hollow site while the benzene group is located near parallel to the surface. The more stable adsorption configuration (I) have the benzene ring centered near an hcp hollow site while the less stable adsorption configuration (II) have the benzene ring centered near an on-top site. The molecule can change adsorption configurations by rotation around the sulphur atom. Rotation from (II) to (I) occurs more rapidly than in the opposite direction. In addition to rotations the molecule can diffuse to nearby adsorption site. The sulphur atom jumps to one of six nearby adsorption sites along the high symmetry axis of Cu(111) while the orientation of the molecule with respect to the substrate remains the same. The rate of rotations and translations has been measured at different temperatures in the range 50-60K. An Arrhenius fit to the measured data yields rotations and diffusion barriers of 120meV, 130meV and 150meV respectively. DFT calculations show good agreement with the STM data. At higher coverages the adsorbed BT molecules from stable aggregates. No stable aggregates larger than 7 molecules were found, instead the density of evenly distributed 7-molecule aggregates increases with the coverage. Abundance histograms of aggregates with different sizes and configurations reveal a delicate balance between molecule-substrate and molecule-molecule interactions.

9:20am **SS+EM-WeM4 Tunneling Spectroscopy of Self-Assembled Monolayers of 1-adamantanethiolate on Single Crystal Metallic Substrates**, A.R. Kurland, A.A. Dameron, P. Han, S.U. Nanayakkara, P.S. Weiss, The Pennsylvania State University

We measure local barrier height and differential conductance using ultrahigh vacuum scanning tunneling microscopy (STM) at 4 K to investigate the work function and local density of states, respectively, of individual adamantanethiolate molecules on a range of single crystal metallic substrates. These techniques allow us to probe specific electronic characteristics while simultaneously resolving the molecular lattice of the adamantanethiolate monolayers. Previously, we have shown that adamantanethiolate molecules form well-ordered hexagonally close-packed monolayers on the Au{111} surface. The complex and highly symmetric cage structure of adamantanethiolate results in weaker intermolecular interactions than those of alkanethiolate self-assembled monolayers. Taking advantage of these properties, we have implemented adamantanethiolate molecules in thin-film molecular lattices and as nanolithography patterning inks. We aim to exploit and to incorporate the unique physical and electronic interactions of adsorbed adamantanethiolate to understand and to tailor self-assembled nanostructures.

9:40am **SS+EM-WeM5 Interaction Pathways of Vapor Deposited Metal Atoms with Self-Assembled Monolayers**, D. Allara, N. Winograd, Pennsylvania State University; A.V. Walker, Washington University; T. Tighe, T. Daniel, O. Cabarcos, S. Uppili, Pennsylvania State University

INVITED

With rapid progress being made in the fabrication and testing of molecule-based electronic devices in the past several years one of the critical issues that has arisen is the character of the metal-molecule interfaces and interphases of vapor-deposited top contact device structures. Results will be discussed that show a broad strategy for developing correlations between the interactions of a wide variety of metals with a range of alkanethiolate/Au{111} self-assembled monolayers (SAMs) carrying varied terminal groups. The metals include inert coinage metals, one-electron donor alkali metal and aggressively reactive metals such as Ti. The SAMs range from those with hydrocarbon surface character to others with high electron acceptor character (-NO@sub 2@, C=N, C=O moieties) and including "solvating" types of groups such as -OCH3. The use of 4-5 different in-situ surface characterization tools augmented by DFT calculations aids greatly in achieving incisive information ranging from metal atom surface scattering to the evolution of the metal-molecule interface chemistry and the metal film morphology. Details include the distribution of metal and reaction products throughout the SAM structure, both laterally and extending to the substrate interface. Coupling this information with the character of the SAM/base electrode interface can provide critical information to aid fundamental interpretations of device behavior.

10:20am **SS+EM-WeM7 Replicative Generation of Electrode Structures by SAM-templated Electrometallization**, I. Thom, G. Haehner, M. Buck, University of StAndrews, UK

Self-assembled monolayers (SAMs) of thiols provide a convenient way to modify electrode surfaces and, thus, to control charge transfer at an

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electrochemical interface. Adjustment of electrode properties from conducting to blocking is achieved by variation of the SAM forming molecules. Since a variety of methods is available to pattern thiol monolayers, this type of SAM can serve as templates to confine electrochemical processes, e.g. metal deposition. However, in addition to the control of charge transfer, SAMs serve also to control adhesion between deposit and electrode and, therefore, make the generation of metal structures by electrochemical deposition and subsequent transfer to a different substrate possible. Copper structures were produced by electrochemical deposition onto SAM-modified polycrystalline gold electrodes. Selective metal deposition was achieved by use of thiols which differ in their electrochemical blocking properties, namely hexadecane thiol and ω -(4'-methyl-biphenyl-4-yl)-methanethiol. After deposition the metal patterns were easily transferred to an insulating substrate by glueing. Characterization of the transferred structures with atomic force microscopy shows that the flatness of the metal surface is essentially determined by the initial SAM carrying substrate electrode. Since the thiol pattern on the substrate electrode remains intact, it can be repetitively used. Therefore, the process allows an easy and fast fabrication of high quality electrode patterns.

10:40am **SS+EM-WeM8 Alkylidyne Self-Assembled Monolayers on Pt(111): A Novel System for Molecular Electronics Applications**, *M. Yang, A.R. Laracuente, L.J. Whitman*, Naval Research Laboratory

Although many alkanethiols form well-understood self-assembled monolayers (SAMs) on gold, such systems are of limited utility for molecular electronics applications given the incompatibility of gold with conventional silicon devices. Moreover, it is now widely recognized that the gold-sulfur bond inhibits electrical transport between the substrate and the bound organic molecules. Because of these issues, there has been recent interest in more compatible metals such as Pd and Pt, along with non-thiol bonding schemes for organic molecules. We are developing a new type of SAM/metal system based on direct carbon-to-metal bonding. When 1-hexene (C@sub6@H@sub14@) is vapor-deposited on clean Pt(111) in ultra-high vacuum, it converts into hexylidyne (C@sub6@H@sub11@) to form a self-assembled monolayer (SAM) with an upright geometry. Scanning tunneling microscopy studies show that the hexylidyne SAM on Pt(111) is a commensurate (3x3) overlayer. We have also investigated the influences of pressure, temperature, and coadsorbed hydrogen on the formation of the alkylidyne SAMs. Given that many of the organic molecules of potential use for current transport are alkanes and perylenes, direct carbon-metal bonding may provide the most desirable metal-molecule junction. Therefore, we believe this system has significant potential for developing molecular electronic devices.

11:00am **SS+EM-WeM9 Vertically Aligned Chromophoric Molecular Assemblies on a Si Surface**, *G.G. Jernigan, M.F. Pepitone, J.S. Melinger, O.-K. Kim*, US Naval Research Laboratory

Strong motivation for the development of molecular devices is the ability to synthetically create a molecule with desired optical and electronic properties through the linkage of different chemical moieties. The challenge remains, however, to integrate such a molecule with a physical device. Molecules can take various physical conformations and can interact with nearby molecules or surfaces resulting in a loss of optical and electronic properties. We have developed a method for encapsulating a 4-[4-(Dimethylamino) styryl]-1-docosylpyridinium bromide (DASP) chromophore in a helical amylose sheath to produce a supramolecular assembly as a molecular device. The benefits of the supramolecular assembly formation are attributed to the ability of the amylose to rigidify the conformation of the DASP molecule, to individually isolate DASP molecules, and to prevent the DASP molecules from interacting with other DASP molecules to form aggregates. When DASP forms aggregates, the fluorescence is quenched, but when DASP is encapsulated by amylose, the fluorescence intensity is maximized. We report that when the supramolecular assemblies are self-assembled onto a Si surface that DASP emits a strong fluorescence with a spectrum that is similar to that found in solution. More importantly, AFM images show that the assemblies vertically self align at near monolayer coverage on the Si surface. We have subsequently linked a viologen species (electron acceptor) to the DASP (electron donor) through various hydrocarbon chain spacers resulting in distant-dependent electron transfer. We report this system as the basis for a molecular photodiode.

11:20am **SS+EM-WeM10 Laser Activation-Modification of Surfaces**, *G. Jiang, M.C. Asplund, M.R. Linford*, Brigham Young University

We have recently developed a new and extremely rapid method for simultaneously functionalizing and patterning surfaces, which we term Laser Activation-Modification of Surfaces, or LAMS. This method consists of wetting a surface, e.g., Si or Ge, with a chemical and firing an intense, nanosecond pulse of laser light (355 or 532 nm) through the liquid onto the surface. The energy ablates a thin layer from the surface, exposing a highly reactive surface that appears to react instantaneously with the liquid it is in contact with. LAMS on silicon has been demonstrated with homologous series of 1-alkenes and 1-haloalkanes, and an epoxide and an alcohol. Unreactive compounds, such as octane and perfluorodecalin, also react in this manner; LAMS on Si with octane results in a functionalized surface. Surface modification is confirmed by X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, and chemical reactivity. Functionalized feature dimensions and morphology are shown by atomic force microscopy and imaging ToF-SIMS.

11:40am **SS+EM-WeM11 Temperature-Dependent Branching of Photochemical Reactions in Organic Layers and Biological Systems**, *M. Zharnikov, A. Shaporenko*, Universität Heidelberg, Germany; *A. Baumer*, Walter Schottky Institut, Germany; *D. Menzel*, Technische Universität München, Germany; *P. Feulner*, Technische Universität München, Germany
Radiation-induced damage represents a severe constraint for the characterization of organic materials, biological macromolecules, and cells by advanced electron or x-ray spectroscopy and microscopy. A possibility to reduce irradiation-induced degradation is cooling of the samples down to cryogenic temperatures. However, although the protecting effect of sample cooling against radiation damage is empirically well demonstrated, no detailed knowledge on its exact microscopic mechanism exists as yet. It is commonly assumed that the main effect is simply hindrance of mass transport in the object, whereas the basic irradiation-induced bond cleavage is believed to be unaffected. To prove this hypothesis we studied radiation damage of self-assembled monolayers, which are prototypes of thin organic layers and highly organized biological systems. We demonstrate that the effect of cooling is twofold. It freezes the structure, but by decreasing the mobility of fragments it also changes the branching of various photochemical reactions, thereby strongly modifying the cross sections as well as the products of irradiation induced processes. Two limiting cases could be identified. Reactions involving transport of single atoms and small fragments proceed nearly independent of temperature. Reactions requiring transport of heavy fragments are, however, efficiently quenched by cooling. We speculate that bonds can recombine if the fragments are forced to stay in place due to their reduced mobility at low temperatures. The results have direct implications for cryogenic approaches in advanced electron and x-ray microscopy and spectroscopy of biological macromolecules and cells.

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