Tuesday Morning, November 16, 2004

Surface Science
Room 210C - Session SS2-TuM

Self Assembled Monolayers

Moderator: M. Grunze, University of Heidelberg, Germany

8:20am **SS2-TuM1 Vapor-Phase Adsorption Kinetics of 1-Decene on Hydrogenated Si(111)**, ***M.R. Kosuri,*** *H. Gerung, Q. Li,* University of New Mexico*; S.M. Han,* University of New Mexico, U. S. A.

We have investigated in situ and in real time vapor-phase self-assembly of 1-decene on hydrogenated Si(111), using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIRS). The p- and s-polarized IR absorbance of Si-H vibrational mode at 2084 cm@super -1@ strongly supports that the Si(111) surface is terminated with monohydrides prior to 1-decene exposure. The adsorption of 1-decene on hydrogenated Si(111) results in a decane terminated hydrophobic surface, indicated by the sessile-drop water contact angle. X-ray photoelectron spectroscopy is additionally used to determine the temperature dependence on self-assembled monolayer (SAM) formation. The decane SAMs prepared at 80 to 200 °C show an identical saturation surface coverage. The absolute surface coverage, calculated from the IR absorbance of C-H stretching vibrational modes near 2900 cm@super -1@ saturates at 4.3x10@super 14@ cm@super -2@, which translates to 55 % of surface Si atom density. The fractional surface coverage of decane indicates that 1-decene adsorption is a two-step process following a 1st order Langmuir isotherm: (1) fast adsorption with an empirical rate constant k@sub 1@ = 4.2x10@super -2@ min@super -1@ and (2) slow adsorption with an empirical rate constant of k@sub 2@ = 1.6x10@super -2@ min@super -1@. The thickness and cant angle of the decane SAM at the saturation coverage are calculated to be 13 Å and 15° from the surface normal, respectively. In this presentation, we will also discuss the stability of decane SAMs against ambient exposure over time.

8:40am **SS2-TuM2 Molecular Monolayers on Single-Crystal and Nanocrystalline Diamond Surfaces**, ***B.M. Nichols,*** University of Wisconsin-Madison*; J.E. Butler, J.N. Russell, Jr.,* Naval Research Laboratory*; R.J. Hamers,* University of Wisconsin-Madison

The chemical stability and electronic properties of diamond make it an attractive substrate for chemical and biological sensing. Recent studies have demonstrated the ability to covalently functionalize nanocrystalline diamond surfaces with molecules bearing a terminal vinyl (C=C) group via a photochemical process under ambient conditions. Here, we report studies of the properties of monolayer films formed on single-crystal diamond(111) and on polycrystalline diamond thin films by this process. XPS measurements on diamond(111) surfaces functionalized with molecules bearing a vinyl group at one end and a fluorine-protected amine group at the other show that the F/C ratio saturates after ~12 hours of reaction, suggesting a self-terminating monolayer. To prove that the molecules are aligned vertically on the surface, we measured the angular dependence of the apparent F/C ratio; this measurement shows that the F atoms are preferentially located at the exposed surface. We find that single-crystal and nanocrystalline samples have similar reaction rates, thereby eliminating the potential role of grain boundaries or graphitic impurities. To characterize the electronic properties, we measured valence-band photoemission spectra and work functions of clean, H-terminated, and molecularly-functionalized diamond(111) surfaces. Our results indicate that the molecularly-modified samples have work functions comparable to the annealed, clean diamond(111) surface, and substantially higher than the H-terminated sample. We will discuss these results and the relationship between the chemical structure, electronic structure, and photochemical functionalization of diamond surfaces.

9:00am **SS2-TuM3 High Resolution Mapping of Compositional Differences and Reactions at Buried Interfaces by Electric Force Microscopy**, *H. Takano,* University of Pennsylvania*; G. Edwards, A.J. Bergren, J. Driskell, R.J. Lipert,* ***M.D. Porter,*** Iowa State University **INVITED**

The ability to interrogate the chemical composition of organic films is of vast importance to many areas in interfacial and surface science (e.g., electrocatalysis, corrosion inhibition, organic electronic devices, and biocompatability). This presentation describes two sets of results that demonstrate the ability of electric force microscopy (EFM) to map compositional differences of organic monolayers buried under thick polymer films. The first example examines the compositional mapping of organic monolayers buried under an ~430 nm film of polystyrene. The underlying adlayer was patterned onto a gold surface using the microcontact printing of CH3(CH2)16SH followed by solution deposition of HO(CH2)16SH. This procedure results in alternating domains of different terminal groups. Results show that the imaging mechanism exhibits sufficient contrast to function as a mapping methodology for buried functional groups. The second example presents the results from monitoring photochemical reactions of polymeric films deposited on organic monolayer-covered metal substrates. UV-light was irradiated on the polymer/monolayer/metal composites through a photomask, resulting in alternating domains. These findings show not only that EFM can distinguish the domains of reacted and non-reacted portions, but also that EFM can provide sufficient contrast as a subsurface mapping technique. Issues related to the imaging mechanism are also examined. Models that explore the fundamental basis of this capability are also discussed.

9:40am **SS2-TuM5 Chemical Engineering of GaAs Surfaces with Aromatic Self-Assembled Monolayers**, ***M. Zharnikov,*** *A. Shaporenko,* Universität Heidelberg, Germany*; K. Adlkofer,* Technische Universität München, Germany*; A. Ulman,* Polytechnic University*; M. Tanaka,* Technische Universität München, Germany*; M. Grunze,* Universität Heidelberg, Germany

Stochiometric GaAs (100) surfaces were functionalized with monolayers of non-substituted and substituted thiol-derived aromatic compounds and the engineered surfaces were studied by several complementary experimental techniques including synchrotron-based high resolution x-ray photoelectron spectroscopy and near edge x-ray absorption fine structure spectroscopy. The aromatic molecules were found to form well ordered and densely packed self-assembled monolayer on these substrates. The attachment to the substrate occurs over the thiolate headgroup while the intact aromatic chains have an upright orientation with an average tilt angle of about 30°. The functionalization of GaAs was found to prevent an oxidation and contamination of the substrate, keeping the GaAs surface in a pristine state. In addition, the wetting properties of this surface could be controlled by the selection of a suitable substitution, e.g. methyl or hydroxy group. The surface engineering of GaAs with functionalized aromatic monolayers can provide a crucial link for combining GaAs-based heterostructures and devices with bio-organic molecular assemblies.

10:00am **SS2-TuM6 Self Assembled Monolayers of Arenethiol Molecules on Cu(111)**, ***K. Wong,*** *K.-Y. Kwon, B.V. Rao, A. Liu, L. Bartels,* University of California, Riverside

The utility of the thiol group on anchoring organic molecules to metal surfaces has been widely recognized. The thiol group makes sufficiently strong bonds with the metal substrate that stable monolayers are formed spontaneously even at room temperature in a solution environment. At low coverages and under ultra-high vacuum conditions isolated thiols exhibit significant surface mobility even at temperatures as low as 80K. We have studied monolayers of thiolphenol (TP) molecules and several halogen substituted para-X-TP derivates (where X is Br, Cl or F) at various coverages. All TPs adsorb with the benzene ring parallel to the surface and do not tilt to a vertical orientation as long as there is sufficient surface area available to accommodate all adsorbed molecules in a horizontal fashion. At such coverages we find a pronounced dependence of the ability of the TPs to form ordered films on the nature of their substitution. The most remarkable differences were found at incomplete coverage where the molecules have space to rearrange themselves into the optimal surface conformation and are not exposed to lateral stress. X-TP molecules form patterns of various degrees of complexity: Br-TP forms a simple (3x4) structure with one molecule per unit cell. Cl-TP films are made up of slightly more complicated unit cells involving two neighboring molecules whose sulfur atoms are located in different (hcp and fcc) Cu(111) hollow sites. F-TP molecule self assemble into a (8x8)R19@super o@ honeycomb pattern consisting of seven molecules per unit cell. Unsubstituted TP and pentafluoro-TP do not form any extended ordered patterns. This suggests that differences in the chemical properties between the para- and the meta-/ortho- substituents of TPs play a crucial role in the pattern formation process. We present a model based on quadrupolar intermolecular interaction to account for these observations.

10:20am **SS2-TuM7 Fabricating Self-Assembled Monolayers of Selenolates on Noble Metal Substrates**, ***A. Shaporenko,*** Universität Heidelberg, Germany*; A. Ulman,* Polytechnic University*; A. Terfort,* Universität Hamburg, Germany*; M. Grunze, M. Zharnikov,* Universität Heidelberg, Germany

Self-assembled monolayers (SAMs) of selenolates can be considered as an alternative to thiolates for fabricating SAMs on noble metal surfaces. To prove this approach, we applied a standard immersion procedure to prepare SAMs from several aliphatic and aromatic selenide and diselenide compounds on gold and silver substrates. The resulting films were characterized by several complementary experimental techniques including infrared refection-absorption spectroscopy (IRRAS), synchrotron based high-resolution X-ray photoelectron spectroscopy (HRXPS), near edge X-ray absorption fine structure spectroscopy, and contact angle measurements. The results suggest a dissotiative mode of monolayer formation from diselenide compounds on both gold and silver. However, in the case of long chain alkylselenides and dialkylselenides, no high quality films were formed. In the case of short chain alkylselenides, semifluorinated alkylselenides, and biphenylselenides, well-defined and densely packed SAMs were fabricated. Only one selenium species, namely selenolate was found in all above-mentioned films on the basis of the Se3d HRXPS spectra. Distinct C1s photoemission peaks were observed and related to well-defined aliphatic or aromatic chain. Characteristic IR absorption bands and X-ray absorption resonances corresponding to intact molecular chains of definite conformation were observed. The information on molecular orientation and packing density was derived.

10:40am **SS2-TuM8 Interface Electronic Structure of Thiol Terminated Molecules on Metals***, **A.N. Caruso**, L.G. Wang, E.Y. Tsymbal, S.S. Jaswal, P.A. Dowben,* University of Nebraska

Thiol terminated molecules may be useful to both molecular electronic and spintronic applications. The orientation and electronic properties of biphenyldimethyldithiol (S-CH@sub 2@-C@sub 6@H@sub 4@-C@sub 6@H@sub 4@-CH@sub 2@-S) adsorbed on Au(111) and polycrystalline cobalt are identified from combined polarization dependent photoemission and inverse photoemission. The stable orientation, bonding site and electronic properties of methylthiolate (S-CH@sub 3@) adsorbed on Au(111) and Co(0001) are found by density functional calculations. Both experiment and theory show a stronger bonding to cobalt over gold surfaces for both thiol terminated molecules. Calculated charge transfer with the substrates to and from the sulfur further confirms bonding and reasoning behind the experimentally found highest occupied to lowest unoccupied molecular orbital gap offset from the Fermi level. Calculations also show that the three-coordinated fcc and hcp hollow sites are most stable for methylthiolate adsorption.

11:00am **SS2-TuM9 Designing Self-assembled Monolayers (SAM) of Thiols: A Study on Lattice Mismatch***, P. Cyganik,* ***M. Buck,*** St Andrews University, UK*; C. Woell,* Ruhr-Universitaet Bochum, Germany

Applications of self-assembled monolayers (SAM) of thiols in, e.g., molecular electronics or electrochemistry are crucially dependent on the extent to which their properties can be controlled. Besides the control of the molecular electronic properties, controlling the structure, i.e., defects and crystallinity, is an issue of equal importance. As for any adsorbate system tailoring of SAMs has to address mismatch between molecular and substrate lattices. Surprisingly, this aspect which is of fundamental importance toward a controlled design of thiol SAMs has received very little attention. The talk presents STM studies on biphenyl based thiols which are characterized by an alkane spacer between the sulphur head group and the aromatic moiety. Within a homologue series of these biphenyl thiols with the spacer varying from 0 to 6 methylene units, intermolecular interactions, molecular orientation, and, thus, packing of the molecules are substantially changing. Contrast variations in scanning tunneling microscopy images reveal lattice mismatch. The way mismatch is accomodated depends strongly on the alkane spacer and, therefore, the achievable structural perfection is varying across the homologue series. The results suggest that a flexible spacer acts as a buffer layer which can accomodate mismatch between the lattice of aromatic moieties and the substrate lattice.

11:20am **SS2-TuM10 Sulfur-induced Nano-restructuring of the Au(111) Surface: A Real-time STM Study***, **M.M. Biener,*** Harvard University*; J. Biener,* Lawrence Livermore National Laboratory*; D. Pinnaduwage, C.M. Friend,* Harvard University

The interaction of sulphur with gold surfaces has attracted considerable interest due to numerous technological applications such as the formation of self-assembled monolayers (SAMs), corrosion inhibition, and sensors. In this work, the interaction of sulfur with Au(111) was studied by real-time scanning tunnelling microscopy (STM) using sulfur dioxide as a source of sulfur. A small fraction of the impinging sulfur dioxide molecules deposit sulphur on the surface. Up to a coverage of ~0.3 ML sulfur forms an ordered adlayer. With further increasing S coverage we observe the formation of a two-dimensional AuS overlayer exhibiting short range order. Gold atoms are removed from the surface and are incorporated into the growing gold sulfide resulting in pit formation. This gold sulfide layer is stable up to ~500 K where it develops long-range order and exhibits a complex Low Energy Electron Diffraction (LEED) pattern. We will present nano-scale, time-resolved movies capturing the sulphur induced restructuring of the Au(111) surface.

11:40am **SS2-TuM11 Comparative UHV-STM Study of Adsorption Structures Formed from a Family of Oligo(phenylene ethynylene)s on Au(111)***, L. Petersen, C. Busse, S. Terkelsen,* ***T.R. Linderoth****, M. Nielsen, K.V. Gothelf, F. Besenbacher,* University of Aarhus, Denmark

To realize the goal of functional structures formed by molecular self-assembly, systematic studies of factors directing the assembly process are required. Using UHV-STM we have performed a comparative study of adsorption structures formed by a family of structurally different, but chemically similar, organic molecules adsorbed on the Au(111) surface. The molecules consist of a central benzene ring with three or two acetylene spokes (para, meta, or ortho) leading to highly conjugated pi-systems of three-spoke, linear, bent, or v-shaped molecular geometry. Each spoke terminates in a tert-butyl substituted salicylaldehyde moiety. Upon adsorption at room temperature (and imaging at ~150 K to reduce molecular mobility), a variety of close-packed phases are observed, most of which can be rationalized by a common motif of molecules adsorbed with their backbone parallel to the surface and with optimized intermolecular side-to-side interaction, most likely through van der Waals coupling. Interesting exceptions to this picture are the linear molecules, which in addition form a more open nano-grid type structure thought to be dominated by intermolecular hydrogen bonding, and the v-shaped molecules where a reduced footprint indicates non-planar adsorption geometry. The described results constitute a platform for ongoing experiments where (i) similar molecules with systematically altered functional moieties are used, e.g. disabling or further encouraging intermolecular hydrogen bond formation, (ii) structures formed through co-adsorption with transition metals (Ni,Fe) are investigated, and (iii) intermolecular covalent cross-linking is induced through co-adsorption with reactive diamines.

Author Index

Bold page numbers indicate presenter