

Surface Science

Room 327 - Session SS+OM-ThA

Self-Assembled Monolayers

Moderator: L. Hanley, University of Illinois at Chicago

2:00pm **SS+OM-ThA1 Non-dissociative Chemisorption of Methanethiol on Ag(110)- A Critical Result for Self-assembled Layer Formation, J.-G. Lee, J. Lee, J.T. Yates, Jr.,** University of Pittsburgh

Three definitive experiments have been performed which show that CH@sub 3@SH does not dissociate upon chemisorption on clean Ag(110). On the clean Ag(110) surface, the adsorption in the first layer occurs at 0.5 ML, producing a (2x1) LEED structure. The undissociated molecule desorbs at ~140 K. Using a 50%-50% mixture of CH@sub 3@SD and CD@sub 3@SH, no evidence of S-H or S-D bond scission by isotope mixing between these molecules is found upon desorption. And finally, when the CH@sub 3@SH molecule is incident on clean Ag(110) surface in the temperature range from 240 K to 400 K, less than 1% of the incident molecules dissociate to produce adsorbed S. In contrast, when a sulfur-poisoned Ag(110) surface is exposed to CH@sub 3@SH, autocatalytic dissociation occurs below 240 K, producing CH@sub 4@, H@sub 2@S and adsorbed S atoms. These results are in striking contrast to the behavior of Cu(110) where CH@sub 3@SH dissociation occurs below 320 K leaving S. These results are of importance in understanding the self assembly of alkanethiol layers on silver where it has been commonly assumed that S-H bond scission occurs at room temperature. This work was supported by DOE-BES.

2:20pm **SS+OM-ThA2 Spectroelectrochemical Studies of Self-Assembled Monolayers of Thiols, I. Thom,** St Andrews University, Scotland; *M. Buck,* St Andrews University, Scotland, UK

Thiol SAMs provide a convenient route to modify electrodes and to serve as templates for directing electrochemical processes. Towards a rational design of thiol SAMs for electrochemical applications the electrochemically induced desorption and adsorption of thiols are studied in-situ using the combination of electrochemistry and non-linear optical techniques. Potential dependent capacitive and faradaic currents are correlated with the second harmonic signal which probes the S-Au bond formation. Studies of alkane thiols and biphenyl based thiols reveal that this correlation is strongly dependent on the electrolyte, i.e. both the penetration of ions into the layer and the desorption mechanism are affected by the electrolyte. In the ethanol case, a change in the desorption mechanism during multiple potential cycling is observed. While the current continuously decreases with increasing number of cycles, the change of the SHG signal remains essentially unaltered and indicates a change in the faradaic process. This change is explained by a transition from thiolate to disulfide formation upon the desorption of thiols.

2:40pm **SS+OM-ThA3 Photoemission Study of Dodecanethiol on Ag(111) and Au(111), H. Geisler,** Xavier University; *J.M. Burst, S.N. Thornburg, C.A. Ventrice,* University of New Orleans; *Y. Losovyj, P.T. Sprunger,* Louisiana State University

Self-assembled monolayers show great promise for use in many technological applications such as in chemical and biological sensing, chemical resists in lithography, corrosion protection, and molecular electronics. However, there are several fundamental properties of these systems that are not well understood. For instance, the adsorption of alkanethiols on Au(111) results in a (@sr@3 x @sr@3)R30° overlayer; whereas, adsorption on Ag(111) results in an incommensurate overlayer even though Au and Ag are isoelectronic and are lattice matched to 0.3%. Although there have been several studies of the geometric structure of thiols on Au(111) and to a lesser extent on Ag(111), there have been very few studies of the electronic structure of these films. Angle-resolved ultraviolet photoelectron spectroscopy studies of the growth of dodecanethiol on Au(111) and Ag(111) have been performed in UHV by vapor deposition. By using vapor deposition, the submonolayer striped phase, full monolayer upright phase, and the multilayer phase can be studied. The monolayer coverage of thiol results in peaks at binding energies of 20 eV, 14 eV, 10 eV, and 7 eV. By comparing the dispersion of the Ag(111) d-band emission for the clean surface to the surface after deposition of a monolayer of thiol, it was determined that there is a loss of order of the Ag surface atoms. Similar measurements for Au(111) reveal that the Au(111) surface remains in an ordered state. This result provides a mechanism for the different adsorption geometries of alkanethiols on Au(111) and Ag(111). Since there is no ordered template of Ag atoms after thiol adsorption, the van der

Waals interaction between the CH@sub 2@ chains dominates, resulting in an ordered, incommensurate overlayer. Measurements of the thiols in the multilayer regime reveal a uniform shift of the thiol peaks to higher binding energy, presumably due to sample charging effects from the insulating nature of these films at 150 K.

3:00pm **SS+OM-ThA4 Short Aromatic Thiols on Cu(111): Initial Adsorption Configuration and the Formation of an Ordered Monolayer, B.V. Rao, K.-Y. Kwon, J. Zhang, A. Liu, L. Bartels,** University of California at Riverside

We present low-temperature scanning tunneling microscope (STM) measurements of the initial orientation of di-chloro-thio-phenol (DCTP) and S-phenyl-thio-acetate (SPTA), a thio-phenol whose sulfur-bound hydrogen is replaced by an acetyl group. The latter is a common practice in order to protect the thiol group during the synthesis of poly-functional organic molecules. This poster compares the impact of the acetyl substitution on the initial steps of the molecules interaction with a Cu(111) surface. DCTP adsorbs at low temperatures (15K) with the sulfur atom at an on-top site and is able to rotate around it. This results in the observation of a flower shaped species on STM images. There are two chiral adsorption configurations which can be distinguished by STM. In contrast, SPTA adsorbs in a position in which both the phenyl and the second carbon of the acetyl group point upward resulting in a double protrusion in STM images. While tunneling electrons of less than 500meV of either bias can cause the abstraction of hydrogen from the thiol group of DCTP, SPTA is stable beyond 1V in tunneling bias. Increasing the coverage by adsorption at nitrogen temperatures, DCTP forms an ordered monolayer consisting of dimers, both of which have the phenyl group lying flat on the surface. The formation of extended islands of the ordered monolayer requires annealing of the sample beyond liquid nitrogen temperatures. Further increase of the coverage results in pronounced protrusion at defect sites of the ordered monolayer, which we interpret as molecules that point the phenyl ring away from the surface. STM resolution on a film consisting entirely of such species is poor; however, it can confirm that an ordered film is formed.

3:20pm **SS+OM-ThA5 Balance of Structure-building Forces in Monomolecular Films: Terphenyl-substituted Alkanethiolates on Noble Metal Substrates, A. Shaporenko,** Universität Heidelberg, Germany; *M. Brunnbauer, A. Terfort,* Universität Hamburg, Germany; *L.S.O. Johansson,* Karlstad University, Sweden; *M. Zharnikov,* Universität Heidelberg, Germany

The design of versatile monomolecular films relies on detailed knowledge of basic rules governing the packing density and exact arrangement of the molecular constituents in these systems. The most important issue in this connection is the understanding of the interplay between the structure-building headgroup-substrate and intermolecular interactions. To address this issue we have studied self-assembled monolayers (SAM) formed from terphenyl-substituted alkanethiols C@sub 6@H@sub 5@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH (TPn, n = 1-6) on Au and Ag substrates. In these systems, strongly interacting terphenyl backbones force a dense molecular packing, which does not fit to the geometry of the metal-S-C bond at certain length of the aliphatic part. We used several complementary experimental techniques such as x-ray photoelectron spectroscopy (XPS), high-resolution XPS, near edge X-ray absorption fine structure spectroscopy, infrared absorption spectroscopy, ellipsometry, and water contact angle measurements to characterize the TPn SAMs. Odd-even changes in the packing density, the tilt angle of the terphenyl moieties, etc have been observed and considered in detail. These changes could be clear correlated with the geometry of the metal-S-C bond, which assumed to be different on Au and Ag. The results imply a predominant role of the headgroup-substrate interaction in the balance of structure-building forces in the aliphatic SAMs and give a practical tool for the fabrication of monomolecular films with desired properties.

3:40pm **SS+OM-ThA6 Pronounced Odd-Even Changes in the Molecular Arrangement and Packing Density of Biphenyl-Based Thiol SAMs: A Combined STM and LEED Study, P. Cyganik, M. Buck,** University of St Andrews, UK; *W. Azzam, G. Witte, Ch. Woell,* Ruhr Universitaet Bochum, Germany

Self-assembled monolayers (SAMs) of thiols are promising candidates for nanolithographic applications. Towards a rational design and control down to the length scale reaching molecular dimensions we study SAMs a particular type of thiols which is characterized by a biphenyl unit and an alkane spacer of varying length (CH@sub 3@(C@sub 6@H@sub 4@)@sub 2@(CH@sub 2@)@sub n@SH, BPn, n = 2, 3, 4, 5). SAMs adsorbed on Au(111) substrates were studied using scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Our results demonstrate

Thursday Afternoon, November 6, 2003

that preparation at elevated temperature results in highly ordered layers with large domains. Whereas the (2@sr@3x@sr@3) structure of the BP3 and BP5 SAMs is similar to that reported previously for other aromatic thiols, SAMs made from BP2 and BP4 exhibit a very different structure. A (5@sr@3x3)rect unit cell containing 8 molecules is found which corresponds to a packing density reduced by 25 % compared to BP3 and BP5. The odd-even effect observed in the molecularly resolved STM images of BPn, therefore, confirms the pronounced influence of the spacer chain on the structure of these biphenyl based SAMs.

4:00pm SS+OM-ThA7 Mechanism of Nanomolecular Motion Induced by Polarity Change of the Electric Field in the Self-Assembled Monolayers, T. Ishida, AIST, Japan; *H. Fukushima*, TPRC, SEIKO EPSON Corporation, Japan; *T. Tamaki*, AIST, Japan

We have successfully observed the nanoscale molecular motion induced by polarity change of the electric field by STM, when small amounts of asymmetrical disulfides containing mobile terphenyl moieties were embedded into pre-assembled dodecanethiol SAMs. Taking the direction of the dipole moment into account, the thickness of embedded molecular protrusions became larger at the positive bias. However, STM experiments revealed that the thickness of the molecular protrusions was larger at the negative bias, contrary to this prediction. STS revealed the higher rectification property at the area of the terphenyl terminated monolayer where also showed the higher electrical conduction at the negative tip bias compared to positive one. The higher electrical conduction at the negative tip bias was likely to retract the STM tip, showing the apparent nanomolecular motion by the polarity change. Next, we investigated the relationship between the higher rectification property and real conformational change. When symmetric disulfide which is not easy to change molecular conformation are embedded into pre-assembled dodecanethiol SAMs for the comparison, both the rectification property and apparent molecular motion were not observed. In addition, when the STM tip was directly attached to asymmetric disulfides, rectification property was not observed in STS. Thus, we concluded that the conformational change is the influential factor to induce the higher rectification property. @FootnoteText@@@footnote 1@ T. Ishida, H. Fukushima, T. Tamaki and H. Tokumoto, Jpn J. Appl. Phys. in press. @footnote 2@ H. Fukushima and T. Tamaki J. Phys. Chem. B106 7142(2002).

4:20pm SS+OM-ThA8 The Reaction of Tetrakis(dimethylamino)titanium with Self-Assembled Monolayers Possessing -OH, -NH@sub2@ and -CH@sub3@ Terminal Groups, A.S. Killampalli, P.F. Ma, J.R. Engstrom, Cornell University

Organic materials are playing an increasing role in modern microelectronic devices--beyond their traditional role as photoresists. New areas include their application as low-@kappa@ dielectrics. Interfaces between organics and metals are also of interest, including in fields such as molecular electronics. To date, almost all work concerning the formation of organic-metal interfaces on pre-existing organic layers has involved metal thin films deposited by (elemental) evaporation. In the work described here we examine an alternative approach to the formation of inorganic-organic interfaces, namely, via the use of organo-transition metal complexes. Here we study the reaction of the titanium precursor, tetrakis(dimethylamino)titanium (TDMAT), with model organic surfaces [self-assembled monolayers (SAMs) terminated by -OH, -NH@sub2@ and -CH@sub3@ groups] using X-ray photoelectron spectroscopy (XPS). Trichlorosilane self-assembled monolayers have been formed on SiO@sub2@ surfaces that, in selected cases, were subjected to additional chemical conversion steps. Prior to insertion into vacuum these layers were characterized using AFM, ellipsometry and contact angle measurements. Exposure of these surfaces to TDMAT was carried out in a custom-designed ultrahigh vacuum chamber equipped with facilities for XPS and quadrupole mass spectrometry (QMS). In selected cases, angle resolved XPS (ARXPS) was used to probe the spatial extent of reaction of the precursor. Among the SAM surfaces studied, the -OH terminated SAM exhibits the highest reactivity, followed by the -NH@sub2@ and -CH@sub3@ terminated SAMs, in that order. ARXPS results reveal that TDMAT reacts primarily at the top of the -OH terminated SAM, while the reaction on the -CH@sub3@ terminated SAM is actually with underlying reactive regions at the SAM/SiO@sub2@ interface. Additional results concerning the reaction of TDMAT with these monolayers, including modeling of the adsorption kinetics, will be presented.

4:40pm SS+OM-ThA9 Characterization of Carboxyl Functionalized SAMs and Surface-Attached Interlocking Molecules Using Near-Edge X-ray Absorption Fine Structure, T.M. Willey¹, University of California, Davis and Lawrence Livermore National Lab; *A.L. Vance, T. van Buuren, C. Bostedt, B.R. Hart, R.W. Meulenberg, A.J. Nelson, L.J. Terminello,* Lawrence Livermore National Laboratory; *C.S. Fadley,* Lawrence Berkeley National Laboratory

Self-Assembled Monolayers (SAMs) and other organo-thiol compounds on Au(111) have become increasingly important to achieve surface attachment of complex molecules. In order to produce useful films, one needs to understand the orientation, order, and substrate bonding of the molecules. Carboxyl and amino terminated SAMs are useful in functionalizing surfaces for surface attachment and immobilization of proteins, DNA, viruses, as well as using the charged state of the endgroups in switchable surfaces. We are also using such functionalization in surface attached interlocking molecules to attempt to induce and measure reorientation (switching) within interlocking molecules. However, functionalization often (adversely!) affects the synthesis, order, packing, and formation of these films. With proper synthetic protocol, many of these issues can be overcome. Here, NEXAFS results probe the orientation of molecules while XPS is used to determine the attachment and chemical nature of the films. We present NEXAFS spectra to compare and contrast the ordering and between SAMs from mercaptohexadecanoic acid (HS(CH@sub 2@)@sub 15@COOH) a long-chain molecule with strong chain-chain interactions and thioctic acid (S@sub 2@(CH@sub 2@)@sub 2@CH(CH@sub 2@)@sub 4@COOH) with a large base hindering strong interactions between its short chains. Stark conformational differences occur in these films of the endgroups with deprotonation (COO- vs. COOH.) In addition, we will present initial results on ordering and attachment in amino-terminated alkanethiols on gold, and preliminary results using functional groups in switching interlocking molecules on surfaces.

5:00pm SS+OM-ThA10 Self Assembled Monolayers on Microelectronic Copper Thin Film for Prevention of Corrosion, Y.S. Tan, National University of Singapore, Singapore; *M.P. Srinivasan, S.O. Pehkonen,* National University of Singapore; *Y.M. Chooi,* Chartered Semiconductor Manufacturing Ltd., Singapore

Abstract: Self-assembled monolayers of dodecanethiol (DT), Mercaptobenzothiazole (MBT), Benzotriazole (BTA) and Imidazole (IMD) were formed by adsorption on the surface of copper thin film used in the ultra large-scale integrated circuits. The films were characterized by X-Ray Photoelectron Spectroscopy (XPS), Fourier Transform Infrared (FTIR) Spectroscopy and contact angle measurements. The corrosion inhibitive behaviours of these organic monolayers were investigated in aerated 0.5 moldm@sup -3@ H@sub 2@SO@sub 4@ solutions by means of Electrochemical Impedance Spectroscopy (EIS) and polarization techniques. The presence of the monolayers reduced corrosion by blocking the copper surface from the dissolved oxygen in the acid medium. The relative inhibition efficiencies of these inhibiting agents in preventing copper oxidation is found to be in the order of: DT > MBT > BTA > IMD. The effectiveness of the inhibitors increased with temperature, concentration of the inhibitors and immersion time in the solution. An adsorption model was proposed on the basis of the variation of impedance with inhibitors' concentration.

Author Index

Bold page numbers indicate presenter

— A —

Azzam, W.: SS+OM-ThA6, **1**

— B —

Bartels, L.: SS+OM-ThA4, **1**

Bostedt, C.: SS+OM-ThA9, **2**

Brunnbauer, M.: SS+OM-ThA5, **1**

Buck, M.: SS+OM-ThA2, **1**; SS+OM-ThA6, **1**

Burst, J.M.: SS+OM-ThA3, **1**

— C —

Chooi, Y.M.: SS+OM-ThA10, **2**

Cyganik, P.: SS+OM-ThA6, **1**

— E —

Engstrom, J.R.: SS+OM-ThA8, **2**

— F —

Fadley, C.S.: SS+OM-ThA9, **2**

Fukushima, H.: SS+OM-ThA7, **2**

— G —

Geisler, H.: SS+OM-ThA3, **1**

— H —

Hart, B.R.: SS+OM-ThA9, **2**

— I —

Ishida, T.: SS+OM-ThA7, **2**

— J —

Johansson, L.S.O.: SS+OM-ThA5, **1**

— K —

Killampalli, A.S.: SS+OM-ThA8, **2**

Kwon, K.-Y.: SS+OM-ThA4, **1**

— L —

Lee, J.: SS+OM-ThA1, **1**

Lee, J.-G.: SS+OM-ThA1, **1**

Liu, A.: SS+OM-ThA4, **1**

Losovyj, Y.: SS+OM-ThA3, **1**

— M —

Ma, P.F.: SS+OM-ThA8, **2**

Meulenberg, R.W.: SS+OM-ThA9, **2**

— N —

Nelson, A.J.: SS+OM-ThA9, **2**

— P —

Pehkonen, S.O.: SS+OM-ThA10, **2**

— R —

Rao, B.V.: SS+OM-ThA4, **1**

— S —

Shaporenko, A.: SS+OM-ThA5, **1**

Sprunger, P.T.: SS+OM-ThA3, **1**

Srinivasan, M.P.: SS+OM-ThA10, **2**

— T —

Tamaki, T.: SS+OM-ThA7, **2**

Tan, Y.S.: SS+OM-ThA10, **2**

Terfort, A.: SS+OM-ThA5, **1**

Terminello, L.J.: SS+OM-ThA9, **2**

Thom, I.: SS+OM-ThA2, **1**

Thornburg, S.N.: SS+OM-ThA3, **1**

— V —

van Buuren, T.: SS+OM-ThA9, **2**

Vance, A.L.: SS+OM-ThA9, **2**

Ventrice, C.A.: SS+OM-ThA3, **1**

— W —

Willey, T.M.: SS+OM-ThA9, **2**

Witte, G.: SS+OM-ThA6, **1**

Woell, Ch.: SS+OM-ThA6, **1**

— Y —

Yates, Jr., J.T.: SS+OM-ThA1, **1**

— Z —

Zhang, J.: SS+OM-ThA4, **1**

Zharnikov, M.: SS+OM-ThA5, **1**