Tuesday Morning, October 3, 2000

Surface Science Room 209 - Session SS2+NS+BI+EL-TuM

Self-Assembled Monolayers

Moderator: D.H. Fairbrother, Johns Hopkins University

8:20am SS2+NS+BI+EL-TuM1 Creating Highly Selective Organic Surfaces using Self-assembly: A New Family of Organothiols, *R. Arnold*, Ruhr-Universität Bochum, Germany; *A. Terfort*, Universität Hamburg, Germany; *C. Wöll*, Ruhr-Universität Bochum, Germany

The creation of organic surfaces with specific properties via the adsorption of correspondingly functionalized organothiols has recently attracted considerable interest, e.g. in the context of bio-sensors and biomimetics. In case of alkanethiols some functional groups, however, interact so strongly with each other that the ordering within the SAMs is affected, e.g. in the case of -COOH functional groups.@footnote 1@ The situation can be improved by using more rigid backbones, e.g. oligophenyl units.@footnote 2@ With regard to biochemical applications in many cases the distance between adjacent organothiol units (4.97 Å) is too small to immobilize larger molecules, e.g. small proteins. In the past these problems could be overcome in some cases by diluting the functionalized organothiol in a shorter, nonfunctionalized thiol. Here, we present a different approach where a more bulky thiol is used, which increases the nearest neighbor distance. We will present the results of a study using several homologues of triptycenethiols. SAMs formed from these compounds were characterized by using XPS, IRRAS, NEXAFS, LEED and TDS. The results reveal the formation of well ordered monolayers, which are anchored to the gold surface in a more distant lateral structure than alkane- or pterphenylthiols. @FootnoteText@ @footnote 1@ Dannenberger, O.; Weiss, K.; Himmel, H.-J.; Jäger, B.; Buck, M.; Wöll, C. Thin Solid Films 1997. 307, 9885-9893 @footnote 2@ Himmel, H.-J.; Terfort, A.; Wöll, C. J. Am. Chem. Soc. 1998, 120, 12069-12074.

8:40am SS2+NS+BI+EL-TuM2 Characterization of the Alkanthiol/Metal Interface by High Resolution Core Level Spectroscopy, K. Heister, H. Rong, M. Buck, University Heidelberg, Germany; L. Johansson, University Karlstad, Sweden; M. Zharnikov, M. Grunze, University Heidelberg, Germany

During the last decade X-ray Photoelectron Spectroscopy with a laboratory X-ray source became a conventional technique to characterize thiol derived SAMs. However, due to the mostly poor energy resolution, a strong attenuation of the photoelectron signal, and a low photoionization crosssection of the relevant core levels at high photon energies a precise binding energy analysis of an important building block of a SAM, the SAM/metal interface was hardly possible, even though high resolution photoelectron spectroscopy could give important information about the chemical state of the atoms in this region. Taking advantage of the high performance and tunebility of the third generation synchrotron sources we have firstly applied the synchrotron-based High Resolution Core Level Spectroscopy to study the SAM/metal interface. The variable photon energy of the synchrotron light and a high energy resolution of the spectrometer (0.1-0.3 eV) enabled us to resolve the bulk and surface components of the substrate emission peak (Au 4f / Ag 3d) and monitor the evolution of these components upon the alkanethiol and biphenylthiol adsorption. Simultaneously, the interaction of the thiol-derived molecules with the substrate was followed by monitoring the S2p doublet attributed to the sulfur head group of these molecules. Only one sulfur species was found in the densely packed SAMs, which implies an equivalent bonding geometry for all adsorbed molecules. In SAMs comprising of specially designed, mixed aliphatic-aromatic molecules a periodical, 'odd-even' shift of the S2p binding energy with the varying length of the aliphatic part was observed. This shift can be attributed to the distortion of the substrate-S bonding angle resulting from the unfavorable package conditions occurring at definite lengths of the aliphatic part. This work has been supported by the German Bundesministerium für Bildung, Wissenschaft und Technologie through grant No. 05 SL8VHA 2 and by DAAD.

9:00am SS2+NS+BI+EL-TuM3 The Influence of the Endgroup and the Chain Length on the Growth of CH@sub 3@- and CF@sub 3@-terminated Alkanetiols on Au(111), J. Pflaum, Princeton University; G. Bracco, University of Genova, Italy; G. Scoles, Princeton University; R. Lee, University of Houston; A. Kahn, Princeton University

The influence of the functional endgroup and the CH@sub 2@ chain length on the growth of alkanethiols on Au(111) was studied by scanning tunneling microscopy (STM) and x-ray surface diffraction in grazing-

incidence geometry (GIXD). Thiols are model systems for self-assembled monolayers (SAMs) and exhibit a complex phase diagram as function of coverage. The structure and the electronic properties of the SAMs are determined by the sulfur headgroup, the CH@sub 2@ backbone and the functional endgroup. Leaving the sulfur headgroup unchanged, we studied how the film structure depends on the endgroup by comparing CH@sub 3@- and CF@sub 3@-terminated thiols. All films were prepared from solution on an atomically ordered Au(111) surface. The lateral order of the as-grown CH@sub 3@-terminated films corresponds to the c(4x2) phase, i.e. the highest density standing-up phase. From STM studies we conclude that the arrangement of CH@sub 3@ endgroups corresponds to a pinwheel-like structure rather than to a zig-zag-like structure. In contrast, CF@sub 3@(CH@sub 2@)@sub 9@SH showed no lateral ordering as seen by STM and GIXD. However, the difference between electron densities at the CF@sub 3@/vacuum and the SH/Au interfaces induces an oscillation of the GIXD reflectivity. Fitting the periodicity of the modulation using the Parratt formalism leads to an estimate of the film thickness and its roughnesses at both interfaces. In spite of the lack of lateral order the film appears to be made by standing-up molecules. Differences between the thickness measured by ellipsometry and x-rays will be discussed. We will also explore the lying-down phase of alkanethiols and fluorinated thiols as organic templates for organic heterostructures. Initial results on the growth of PTCDA on such templates will be presented. This work was supported by the MRSEC program of the National Science Foundation (DMR-9809483). J.P. thanks the Deutsche Forschungsgemeinschaft for support (Grant No. PF 385/1-1).

9:20am SS2+NS+BI+EL-TuM4 Self-Assembled Monolayers of Terphenyl Derivatized Thiols; Adsorption, Insertion Process and Electrical Conduction, *T. Ishida*, JRCAT-NAIR and PRESTO-JST, Japan; *W. Mizutani*, JRCAT-NAIR, Japan; *N. Choi*, JRCAT-ATP, Japan; *H. Tokumoto*, JRCAT-NAIR, Japan

The investigation of SAMs made from conjugated molecules is highly activated from a viewpoint of molecular electronics as well as stable SAM formation. In the present study, we have investigated an insertion process of conjugated molecules, terphenylthiol (TPO), terphenyl methanethiol (TP1), terphenyl propanethiol (TP3), into nonanethiol self-assembled monolayers (SAMs) on Au(111) by STM. STM observation revealed that the insertion process is dependent on the molecular length of conjugated molecules. At the initial stage of insertion, replaced area of TP1 is larger than those of TPO and TP3. However, when the immersing time is more than 12h, the replaced area of TP3 is larger than those of TP0 and TP1. The insertion process is likely to be determined by the solubility of the conjugated molecules and thermal dynamics. The single molecular resistance were increased with the number of the methylene groups, and obtained about 20G-ohm (TP0), 40 G-ohm (TP1) and 66 G-ohm (TP3). The vertical conduction of the conjugated molecular domains of TP1 and TP3 depended on their lateral sizes, while strong dependence was not observed in the case of TPO, suggesting that methylene group is necessary between the sulfur and aromatic rings to increase the vertical conduction of molecular domain.

9:40am SS2+NS+BI+EL-TuM5 Structure and Chemistry of Alkanethiol Self-Assembled Monolayers, G.E. Poirier, T.M. Herne, C.C. Miller, M.J. Tarlov, National Institute of Standards and Technology INVITED Derivatized alkanethiols form dense, physically blocking films on Au surfaces thereby providing an effective and parsimonious method to control the chemical, physical, and electron-transfer properties of electrode surfaces. To predict the function of these monolayers in device applications, scientist require an understanding the molecular-scale structure and chemistry. Our structure studies were conducted using gasphase transport of decanethiol onto clean Au(111). Characterization was accomplished using ultrahigh vacuum scanning tunneling microscopy. At low surface coverage, decanethiol exists as a 2-dimensional 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 (striped phases). Above saturation coverage of the densest striped phase, the monolayer undergoes an edge-mediated melting transition forming a supercooled 2dimensional liquid. Domains of the c(3x2*3) phase, characterized by alignment of the molecular axes close to the surface normal, nucleate and grow from this surface liquid. The reaction of these monolayers with ozone was characterized using scanning tunneling microscopy and x-ray photoelectron microscopy; our results show that exposure to ozone results in oxidation of the thiol terminus. The reaction initiates at the c(3x2*3) domain boundary network and propagates into the domains. Above a

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threshold surface oxygen content, the monolayer converts to a twodimensional fluid that can subsequently recrystallize to a commensurate monolayer of partially oxidized thiol. Further exposure to ozone results in conversion of the monolayer to a fluid phase and a 10% to 30% expansion of the Au lattice at the Au-thiol interface with concomitant formation of Au islands. Our results demonstrate that crystallographic defects in monolayer films can play an important role in their chemical reactions.

10:20am SS2+NS+BI+EL-TuM7 Characterization of SAMs with Contrast Variation SPR Technique, K. Tamada, NIMC and RIKEN Frontier Program, Japan; H. Akiyama, J. Nagasawa, NIMC, Japan

We report characteristics of azobenzene-containing self-assembled monolayers (SAMs) which is designed and synthesized for surface photoisomerization reaction. The surface reaction was monitored by Surface Plasmon Resonance Spectroscopy (SPR), in which the contrast variation technique with various organic solvents was used to improve the accuracy for determination of the optical thickness change by surface reaction. The SAM formation was monitored by kinetic mode experiment with SPR in 0.1mM hexane solution, and after rinsing, refractivity change by UV-VIS photo irradiation was studied in various solvents. In this study, hexyl azobenzene thiol (12-(4-((hexylphenyl)azo)phenoxy)dodecane-1-thiol) SAM was used as an unreactive surface and unsymmetrical azobenzenedisulfides SAMs with the same azobenzene functions were used as reactive ones. Following the previous reports, monomeric dispersion of dye function with disordered chains seems to be necessary to realize highly reactive surface. For our unsymmetrical azobenzene-disulfides SAMs, the free volume for photo-isomerization reaction are guaranteed by 50% dilution of dye functions on surface at monomolecular level. As a result, it was confirmed that unsymmetrical azobenzene-disulfides SAMs were highly reactive, especially, in good solvents (alkanes: C5, C6, C7, C8) and the length of alkyl side chains was quite efficient for surface reactivity.

10:40am SS2+NS+BI+EL-TuM8 Characterization of a Polymerized Self-Assembled Monolayer Using NEXAFS, A.L. Marsh, D.J. Burnett, University of Michigan; D.A. Fischer, National Institute of Standards and Technology; C.E. Evans, J.L. Gland, University of Michigan

Near-edge X-ray Absorption Fine Structure, or NEXAFS, at the C-K-edge was used to characterize the orientation of the polymeric backbone in a selfassembled monolayer of 15,9-polydiacetylene. Monolayers were fabricated from the assembly of molecules of dinonacosa-10, 12-diyn-disulfide from a chloroform solution onto a 2000 Angstrom gold film on a mica substrate. Polymerization occurs across one of the C-C triple bonds in the chain, which results in a polymeric network located within the monolayer. Since resonance intensities in NEXAFS spectra are dependent on electric dipole selection rules, it is possible to determine the orientation of the polymeric backbone by comparing spectra at normal incidence (E vector parallel to the surface plane) with spectra at glancing incidence (E vector perpendicular to the surface plane). From the two spectra it was determined that the polymeric backbone is oriented parallel to the surface, while the alkyl chains are oriented perpendicular to the surface. Since NEXAFS probes unfilled molecular orbitals, it is capable of distinguishing between various bonds, i.e. a C-C double bond versus a C-C triple bond, making it possible to determine structural changes as a function of temperature. Upon increasing the temperature, the C-C double bond pi* resonance increases, while the C-C triple bond pi* resonance decreases. These changes would be consistent with a degradation of the polymer backbone. Above a threshold temperature, the changes are irreversible, leading to eventual thermal degradation of the monolayer.

11:00am SS2+NS+BI+EL-TuM9 An Estimation of Effective Mean Free Path of Photo- and Auger Electrons in Partial Yield Measurements using Selfassembled Monolayers, *M. Zharnikov*, *S. Frey, K. Heister, M. Grunze*, Universität Heidelberg, Germany

In the partial electron yield (PEY) acquisition mode commonly used in X-ray absorption spectroscopy both elastically and inelastically scattered electrons contribute to the signal with the latter contribution presumably dominating. In this case a majority of inelastic scattering events will not result in the signal attenuation as it happens in the X-ray photoelectron spectroscopy (XPS). The scattered electrons will still have a kinetic energy in the acquisition range of the spectrometer. The related values of mean free path (MFP) should be, therefore, noticeably larger than the wellknown inelastic mean free paths for electrons of definite kinetic energy. We have performed XPS and near edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements for series of self-assembled monolayers of alkanethiols on gold substrate. The length of the alkyl chain and, subsequently, the film thickness was varied. In agreement with the expectations, the obtained effective MFPs for the Au 4f photoelectrons and C@sub KLL@ Auger electrons in the PEY acquisition mode exceed the respective values for the elastically scattered electrons of the same kinetic energies (the Au 4f and C@sub KLL@ electrons made up the elastic component of the acquired PEY signals). Furthermore, the PEY-MFP for the C@sub KLL@ Auger electrons increased with decreasing retarding voltage of the PEY detector, which correlates with the increasing contribution of the inelastically scattered electrons in the acquired signal. The obtained results are of importance for the analysis of NEXAFS spectra in both self-assembled monolayers and polymers. This work has been supported by the German Bundesministerium fuer Bildung, Wissenschaft und Technologie through grant No. 05 SF8VHA 1 and by the Fonds der Chemischen Industrie.

11:20am SS2+NS+BI+EL-TuM10 Growth Process and Thermal Stability of Semifluorinated Alkanethiol Self-Assembled Monolayers on Au(111), *M. Hara*, Frontier Research System, RIKEN, Japan; *A. Suzuki*, Tokyo Institute of Technology, Japan; *K. Tamada*, National Institute of Materials and Chemistry, Japan; *H. Fukushima*, Seiko Epson Co., Japan; *T.R. Lee*, University of Houston

Growth process and thermal stability of semifluorinated alkanethiol (CF@sub 3@(CF@sub 2@)@sub m@(CH@sub 2@)@sub n@SH) selfassembled monolayers (SAMs) on Au(111) have been investigated by thermal desorption spectroscopy (TDS) and scanning tunneling microscopy (STM). The growth kinetics showed nearly the Langmuir adsorption isotherm and the etch pits were formed in the upright phase, while the striped phases were not observed in the initial growth stage for shorter (CH@sub 2@)@sub n@ semifluorinated SAMs. In TDS, no significant peaks can be obtained for dimer molecules and decomposed species, suggesting no associative desorption nor dimerization and thermal stability of the semifluorinated molecules during heating up to 650 K. Since longer (CH@sub 2@)@sub n@ semifluorinated SAMs remained the same chemisorbed state in the monolayer after annealing at around 480 K, it has been confirmed that also the alkyl chain part plays an important role for the thermal stability and the ordering in the semifluorinated alkanethiol SAMs. Following those results, we propose more detailed surface phase transition model of semifluorinated alkanethiol SAMs in the growth and annealing processes.

11:40am SS2+NS+BI+EL-TuM11 Multi-technique Study of Self-Assembled AuCN Monolayers on Au(111) Formed by Electrochemical Deposition, T. Yamada, Waseda University, Japan; R. Sekine, Shizuoka University, Japan; T. Sawaguchi, AIST/MITI, Japan

Two kinds of monolayers of AuCN electrodeposited on Au(111), indexed (1.15x@sr@3R-30°) and (1.41x2@sr@3R-30°), have been investigated by XPS, UPS and HREELS as well as LEED, AES and STM to determine the geometrical, electronic and vibrational properties. Electrodeposition was performed in an aqueous 1 mM KAu(CN)@sub 2@ solution by applying an electrode potential about 0 - +0.1 V vs SCE on the Au(111) crystal. Sharp LEED patterns were obtained for these two kinds of adlavers. AES indicated that both of these adlayers were composed Au, C and N without impurity. Well ordered adlattices composing domain structures (domain size ca. 10 nm) were observed by STM. XPS yielded Au 4f signals from AuCN indicating small fractional positive charges on the Au atom incorporated in AuCN. The UPS of AuCN/Au(111) was composed of the Au orbitals and weak signals from CN orbitals, assigned by relativistic DV-Xa molecular orbital calculation. The binding energies of CN orbitals are in the order of 4@sigma@ > 5@sigma@ > 1@pi@, which indicates that the C-Au bond is essentially covalent. HREELS yielded vibrational spectra similar to that obtained for AuCN crystalline powder.@footnote 1@ The C-N stretching frequencies were found to be 2140-2160 cm@super -1@, which are consistent with the covalent nature of the C-Au bond. In the frequency region below 300 cm@super -1@, loss peaks related to the Au-N bonds were seen. The (1.15x@sr@3R-30°) adlayer is concluded to be composed of -AuCN- linear chains (polymer chains) that are identical to those embedded in the AuCN crystal. For the (1.41x2@sr@3R-30°) adlayer, HREELS indicated distortion or breaking of Au-N bonds. Some structural models are proposed for this. These results reveal a special inorganic polymeric feature of the self-assembled AuCN adlayers lying parallel along the surface. @FootnoteText@ @footnote 1@G. A. Bowmaker, B. J. Kennedy and J. C. Reid, Inorg. Chem. 37, 3968 (1998).

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